OPTIMAL DESIGN OF FLOW CHEMICAL REACTORS WITH COMPLEX GEOMETRY

by

DANIEL YAW-CHUNG KO

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Approved by:

Liang-tseng Fan
Major Professor

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1. INTRODUCTION

Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through a succession of treatment steps. The raw materials undergo a number of physical treatment steps to put them in a form in which they can be reacted chemically. They then pass through the reactor. The products of the reaction must then undergo further physical treatment (separations, purifications, etc.) for the final desired product to be obtained.

The chemical treatment step is often the heart of the process, the thing that makes or breaks the process economically. Design of the reactor is no routine matter, and a great variety of designs can often be proposed for a process. In searching for the optimum design it is not just the cost of the reactor that must be minimized.

Most chemical plants consist of a large number of inter-connected process units which together form a topologically complex system (a system with branches and loops). The chemical reactors are often arranged in such a way. To obtain the optimal design of a geometrically complex process, we have to select the optimal process parameters, and operating variables according to a certain performance criterion (objective function). Many methods, e.g. differential calculus, calculus of variations, linear and non-linear programming, dynamic programming, and the maximum principle have been developed to solve these optimization problems. Most of them, however, are not suitable for practical use when the processes become geometrically complex and the process variables increase. Dynamic programming and the maximum principle were derived and have been greatly extended to attack such geometrically complex and multi-variable processes.

The maximum principle was first developed for simple continuous processes by the Russian mathematician Pontryagin [1]. Katz [2, 3] has presented a discrete version of the maximum principle for simple homogeneous systems. Jackson [4] has pointed out that Katz's algorithm is only true as a "weak algorithm". This so-called "local weak maximum principle" or "stationary principle" only relates stationary values for the discrete case. The extension of Katz's results by Fan and Wang [5, 6, 7] to systems topologically more complex than a simple sequential chain is also only a weak algorithm relating stationary values. Fan and Wang [8] have extended and generalized the continuous maximum principle so that it can be used to optimize topologically or geometrically complex continuous processes. Several other successful attempts to "generalize" the discrete, the continuous, and the composite versions of the maximum principle for complex processes have also been reported [9, 10, 11].

The underlying idea of dynamic programming, first introduced by Bellman [12] is represented by the principle of optimality, which states, "An optimal policy has the property that whatever the initial state and initial decision are, the remaining decisions must constitute an optimal policy with regard to the state resulting from the first decision" [12]. By means of this principle and the method of interpolation, a multistage decision problem is replaced by a sequence of single stage decision problems, for which the solution is drastically simplified. Using the methods of dynamic programming, Aris has solved a variety of problems concerned with optimal chemical reactor design [13]. Based on the dynamic programming technique, Mitten and Nemhauser [14], Aris [15] and Chien [16] have presented several schemes for the optimization of certain types of topologically complex processes. Aris, Nemhauser and Wilde [17] presented a method for formulating cyclic and branching processes as initial value, final value or two-point-boundary value problems. Larson [18] has developed a new approach to attack the problems of continuous characteristics, called dynamic programming with continuous independent variables (State Increment Dynamic Programming). This procedure has a high-speed memory requirement several orders of magnitude less than that of conventional dynamic programming, but it still retains the general applicability and other desirable features of the conventional method.

The principal purpose of this thesis is to show how the maximum principle and conventional dynamic programming can be applied to topologically complex chemical processes, particularly to flow type chemical reactor systems. The study is divided into two parts. The first part is an investigation of optimal temperature profiles in a series of plug flow reactors with either fresh feed to or intermediate product withdrawal from an internal point. A first-order consecutive irreversible reaction $A \longrightarrow B \longrightarrow C$ is taking place in the reactors. A split type, two-point-boundary value problem, which is encountered, is solved numerically. The second part deals with the combined use of the maximum principle and dynamic programming. General working equations for a sequential union of these two techniques are developed. The use of this union will be illustrated by two chemical rate processes with geometrically complex features.

2. THE MAXIMUM PRINCIPLE

The maximum principle was first proposed by a Russian mathematician, Pontryagin [1], in 1956. Pontryagin's original method was confined to simple continuous processes, that is, processes without any geometrically complex structure that may be described by a system of first order differential equations. Many of the processes encountered in practice are, however, composed of several inter-connected branches. Although the optimal policy for such a complex process can sometimes be obtained by disecting the process into several simple subprocesses, independently optimizing each subprocesses, and then recombining these into the overall optimal policy, it is more desirable to use an algorithm capable of obtaining directly the optimal policy for the entire process without decomposing the process. The following essentially follows Fan and Wang [8].

a. Algorithm for Continuous Complex Processes [8]

Schematic representations of two types of continuous complex processes are shown in Figures 1 and 2. Figure 1 shows a continuous complex process involving a separating point, that is, a point where one branch of the path splits into several branches. Figure 2 shows a complex continuous process involving a combining point. A combining point is a point where several branches combine into one single branch. Suppose that each branch in a complex process is described by a performance equation of the following type

$$\frac{dx_i}{dt} = f_i\ (x_1, \ldots, x_s;\ \theta_1, \ldots, \theta_r) \tag{1}$$

$$i = 1, 2, \ldots, s \quad , \quad 0 \leq t \leq T$$

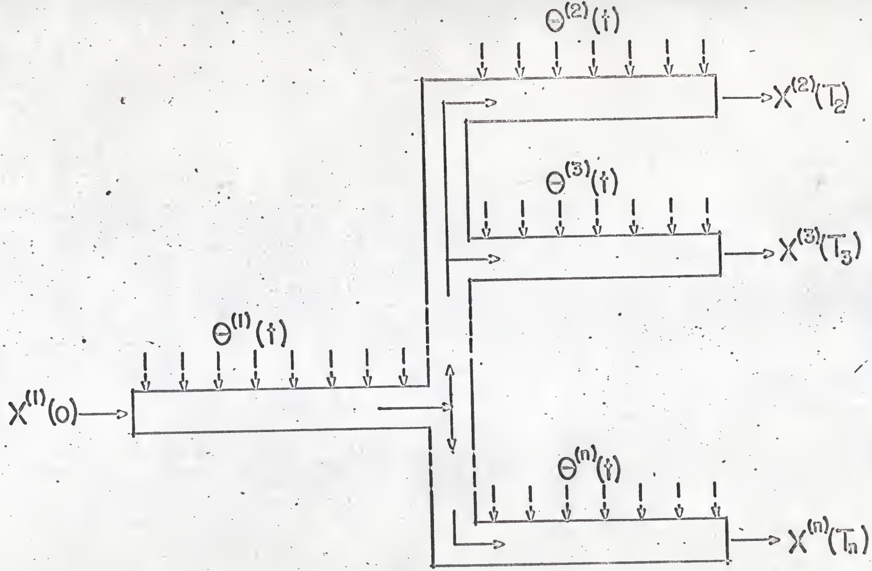

Fig. 1 Separating point.

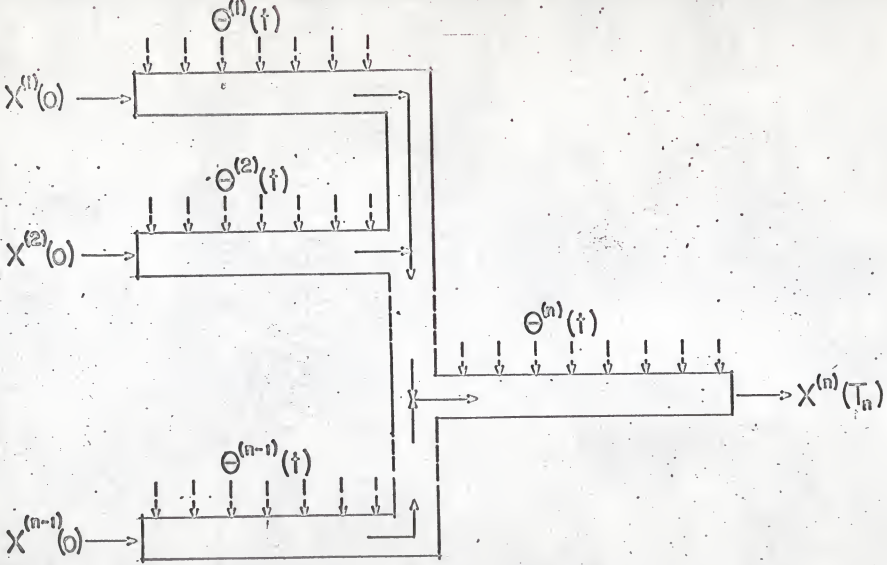

Fig. 2 Combining point.

or in vector form

$$\frac{dx}{dt} = f(x;\theta) , \qquad 0 \leq t \leq T \tag{2}$$

In equation (1), s and r are the dimensions of the state vector x and the decision vector θ respectively. The form of the function, $f(x;\theta)$, and the length or time, may differ for different branches. A number may be arbitrarily assigned to each branch for convenience. The superscripts in $f^{(k)}(x^{(k)};\ \theta^{(k)})$ and the subscript of T_k represent the branch number.

The arrows at the junction point show the direction of the flow of the process streams. The relationships at the junction points between the state vectors of different branches are described by the "junction equations". These are (all the branch numbers are referred to Figures 1 and 2):

(1) Separating points

$$\begin{aligned} x^{(2)}(0) &= g^{(2)}(x^{(1)}(T_1)) \\ x^{(3)}(0) &= g^{(3)}(x^{(1)}(T_1)) \\ &\vdots \\ x^{(n)}(0) &= g^{(n)}(x^{(1)}(T_1)) \end{aligned} \tag{3}$$

(2) Combining points

$$x^{(n)}(0) = g^{(n)}(x^{(1)}(T_1),\ x^{(2)}(T_2), \dots,\ x^{(n-1)}(T_{n-1})) \tag{4}$$

where the function $g^{(n)}(x^{(k)}(T_k))$ is the vector form of $g^{(n)}(x_1^{(k)}(T_k),$ $x_2^{(k)}(T_k), \dots,\ x_{s^{(k)}}^{(k)}(T_k))$. It may be noted that the dimensions of the state vector may be different from branch to branch. Superscripts, such as in $s^{(k)}$, are used to distinguish the differences.

In a complex process, there may be some branches which don't have decision action, such as the fresh feed stream or the bypass product stream at the internal point of a series of tubular reactors. The performance equation for such a non-decision branch is

$$\frac{dx}{dt} = f(x) \tag{5}$$

or for the special case in which the state vector remains constant, equation (5) reduces to

$$\frac{dx}{dt} = 0 \tag{6}$$

A complex process may have several initial points and final points and the values of the state vectors at these points are called initial states and final states respectively.

The optimization problem under consideration may be stated as follows: Given all of the performance equations, junction equations, lengths (or times), and initial states of a complex process consisting of a path with N branches, b initial points, and f final points, find the decision vector function of each branch so as to maximize a certain linear function of the final states of the process, such as

$$\sum_{k=1}^{f} \sum_{i=1}^{s^{(k)}} c_i^{(k)} x_i^{(k)}(T_k),$$

where the summation is over all the components of the state vectors and over all the final states. The set of the decision vector function $\theta^{(k)}(t)$, $k = 1, 2, \ldots, N$, thus found is called the optimal policy. The function to be maximized is called the objective function.

The procedure to find the optimal policy for a complex process can be divided into two steps:

Step 1. Introduce an adjoint vector, $z^{(k)}(t)$, and a Hamiltonian function

$H^{(k)}(x, z, \theta)$ for each branch satisfying:

$$H^{(k)}(x, z, \theta) = \sum_{i=1}^{s^{(k)}} z_i^{(k)} f_i^{(k)}(x_1^{(k)}, \ldots, x_{s^{(k)}}^{(k)}; \theta_1^{(k)}, \ldots, \theta_{r^{(k)}}^{(k)}) \qquad (7)$$

$$\frac{dz_i^{(k)}(t)}{dt} = - \frac{\partial H^{(k)}(x,z,\theta)}{\partial x_i^{(k)}}, \qquad i = 1, 2, \ldots, s^{(k)} \qquad (8)$$

with the values of $z_i^{(k)}$ at the junction points and final points satisfying

(a) separating points

$$z_i^{(1)}(T_1) = \sum_{k=2}^{n} \sum_{j=1}^{s^{(k)}} \frac{\partial g_j^{(k)}}{\partial x_i^{(1)}} z_j^{(k)}(0), \qquad i = 1, 2, \ldots, s^{(1)} \qquad (9)$$

(b) combining points

$$z_i^{(k)}(T_k) = \sum_{j=1}^{s^{(n)}} \frac{\partial g_j^{(n)}}{\partial x_i^{(k)}} z_j^{(n)}(0); \qquad \begin{matrix} i = 1, 2, \ldots, s^{(k)} \\ k = 1, 2, \ldots, (n-1) \end{matrix} \qquad (10)$$

(c) final points

$$z_i^{(k)}(T_k) = - c_i^{(k)}; \qquad \begin{matrix} i = 1, 2, \ldots, s^{(k)} \\ k = 1, 2, \ldots, f \end{matrix} \qquad (11)$$

Step 2.: Find the decision vector function, $\theta^{(k)}$, from the following conditions

$$H^{(k)}(x,z,\theta) = \text{minimum at every point } t, \quad k = 1, 2, \ldots, N \qquad (12)$$

In other words, the optimal functions, $\bar{\theta}^{(k)}$, are obtained by varying $\theta^{(k)}$ until the minimum value of $H^{(k)}$ is attained at each point. The proof of this algorithm is given by reference [8].

3. APPLICATIONS TO FLOW CHEMICAL REACTORS

It is known that for a single reaction, e.g., the first order reversible reaction $A \rightleftarrows B$, taking place in a plug flow reactor, the best yield is obtained if the temperature is so adjusted as to make the reaction rate as large as possible at each point of the reactor. This is the so-called disjoint property of temperature for a single reaction [13]. In the case of two or more competing reactions this is no longer true. The problem of a first order irreversible consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ has been extensively discussed in the work of Bilous and Amundson [19]. They derived equations to be solved simultaneously with reaction equations to give the optimum temperature profile. They use two methods, the first based on an explicit solution of the reaction equation, and the second an implicit method which may be applied to the reaction equations themselves. Both involve, however, the rather difficult notions of functional differentiation, and they really left the problem unsolved. Aris [13] continued the work by the method of dynamic programming. Using the dynamic programming technique, he obtained, by a lengthy derivation and explanation, a set of characteristic equations, which can be easily obtained by direct use of the maximum principle. Most of his work [13] was essentially a qualitative analysis, as he did not obtain a solution of the derived equations. Lee [20] treated this problem by the combined use of the maximum principle and a maximum-seeking method on the analog computer. In his work, the minimum of the Hamiltonian is sought directly by a random search technique.

All of the work described above, however, was confined to the investigation of the optimal temperature and concentration along a single plug-flow reactor. If there are two plug flow reactors arranged in series with product withdrawal from the first reactor, or fresh feed into the second reactor, the optimization problem can't be treated routinely. This geometrically complex arrangement of reactors will render the problem more complicated and difficult, especially with respect to the numerical solution. The reactor arrangements (or models) encountered in this investigation may often be found in industry. It is often desirable, for economic or practical reasons, to use two reactors in series, each with a smaller reactor volume instead of using one large reactor. Also, when we need a certain amount of product with lower conversion, or when we have two sources of raw materials, different both in composition and availability, we might have to set up the reactors in the way shown in either Figure 3 or arranging two tubular reactors in series with fresh feed fed to an internal point.

a. Two Tubular Flow Reactors in Series with Intermediate Product Withdrawal.

Consider a complex continuous process consisting of two tubular flow chemical reactors connected in series with exit flow from an intermediate point, as shown in Figure 3. The reactions taking place in the reactors are considered to be first order irreversible consecutive reactions of the type $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. The length of reactors, L_1 and L_2, and the cross-sectional areas $A^{(1)}$ and $A^{(2)}$ are all specified, that is, the volumes of the two tubular reactors are fixed, or alternatively the holding time of each reactor is fixed for specified volumetric flow rates of feed and intermediate product streams. It is desired to maximize the total amount of product B from the intermediate and end product streams. An equivalent objective function is to maximize the concentration of B at the ends of

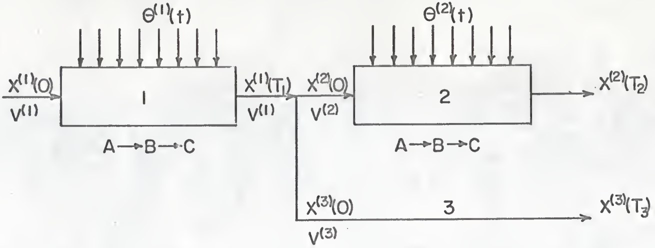

Fig.3 Schematic diagram of two tubular reactors connected in series with product withdrawn from the intermediate point for the reaction $A \rightarrow B \rightarrow C$.

both reactors, since the volumetric flow rate of each stream is fixed. The flows in the reactors are assumed to be plug flows, i.e., it is assumed that a velocity gradient in the radial direction and diffusion in the radial and in the axial directions do not exist in the reactors.

The steady state differential material balance for reactant i in the differential section $d\ell$ of the kth branch, k = 1, 2, can be written as

$$\left\{\begin{array}{l}\text{Rate of input of component i to the differential section } d\ell \\ \text{of the kth branch}\end{array}\right\}$$
$$-\left\{\begin{array}{l}\text{Rate of output of component i from the differential section} \\ d\ell \text{ of the kth branch}\end{array}\right\}$$
$$+\left\{\begin{array}{l}\text{Rate of production of component i in the differential section} \\ d\ell \text{ of the kth branch}\end{array}\right\}$$
$$= 0$$

The derived equation is

$$\left\{v^{(k)}x_i^{(k)}\right\} - \left\{v^{(k)}x_i^{(k)} + v^{(k)}\frac{dx_i^{(k)}}{d\ell}\,d\ell\right\} + A^{(k)}d\ell\left\{R_i^{(k)}\right\} = 0$$

or

$$\frac{dx_i^{(k)}}{d\ell} = \frac{A^{(k)}}{v^{(k)}}\,R_i^{(k)}\,, \qquad i = 1,\ 2,\ \text{and}\ \ k = 1,\ 2 \tag{12}$$

where

$x_i^{(k)}$ = molar concentration of reactant i in the kth branch

$v^{(k)}$ = volumetric flow rate in the kth branch

$A^{(k)}$ = cross sectional area of plug flow reactor in the kth branch

$R_i^{(k)}$ = rate of production of component i in the unit volume

ℓ = axial position in the plug flow reactor (measured from the inlet)

If x_1 and x_2 are the molar concentrations of A and B respectively, the performance equations for each branch can be written, according to equation (12), as

$$\frac{dx_1^{(1)}}{d\ell} = \frac{A^{(1)}}{v^{(1)}} \left\{R_1^{(1)}\right\} \tag{13}$$

$$\frac{dx_2^{(1)}}{d\ell} = \frac{A^{(1)}}{v^{(1)}} \left\{R_2^{(1)}\right\} \tag{14}$$

$$\frac{dx_1^{(2)}}{d\ell} = \frac{A^{(2)}}{v^{(2)}} \left\{R_1^{(2)}\right\} \tag{15}$$

$$\frac{dx_2^{(2)}}{d\ell} = \frac{A^{(2)}}{v^{(2)}} \left\{R_2^{(2)}\right\} \tag{16}$$

Since the mechanism of reaction is the same for both branches 1 and 2, one can write

$$R_1^{(k)} = - k_1^{(k)} \, x_1^{(k)} \tag{17}$$

$$R_2^{(k)} = k_1^{(k)} \, x_1^{(k)} - k_2^{(k)} \, x_2^{(k)} , \qquad k = 1, 2 \tag{18}$$

where k_1 and k_2 are temperature dependent specific reaction rate constants of the Arrhenious type given as

$$k_1 = k_{10} \, e^{-\frac{E_1}{R\theta}} \quad , \qquad k_2 = k_{20} \, e^{\frac{E_2}{R\theta}} \tag{19}$$

where

k_{10} = frequency factor, hr^{-1}

E_i = activation energy, cal/mole

θ = temperature, ^{o}K

R = gas constant, cal/mole ^{o}K

If the holding time is defined as $t = \frac{\ell}{v/A}$, substitution of equations (17) and (18) into equations (13) through (16) yields

$$\frac{dx_1^{(1)}}{dt} = - k_1^{(1)} x_1^{(1)} , \qquad x_1^{(1)}(0) = \alpha_1 \tag{20}$$

$$\frac{dx_2^{(1)}}{dt} = k_1^{(1)} x_1^{(1)} - k_2^{(1)} x_2^{(1)} , \qquad x_2^{(1)}(0) = \alpha_2 \tag{21}$$

$$\frac{dx_1^{(2)}}{dt} = - k_1^{(2)} x_1^{(2)} \tag{22}$$

$$\frac{dx_2^{(2)}}{dt} = k_1^{(2)} x_1^{(2)} - k_2^{(2)} x_2^{(2)} \tag{23}$$

where α_1 and α_2 are the inlet concentration of A and B respectively.

Since no transformation is taking place and no control action is imposed on branch 3, the performance equations for that branch are

$$\frac{dx_1^{(3)}}{dt} = \frac{dx_2^{(3)}}{dt} = 0 \tag{24}$$

Since the outlet stream of component i from reactor 1 splits into two streams at the separating point, the concentration of component i in both streams at this junction must be equal, that is,

$$x_1^{(1)}(T_1) = x_1^{(2)}(0) \tag{25}$$

$$x_1^{(1)}(T_1) = x_1^{(3)}(0) \tag{26}$$

$$x_2^{(1)}(T_1) = x_2^{(2)}(0) \tag{27}$$

$$x_2^{(1)}(T_1) = x_2^{(3)}(0) \tag{28}$$

where

$$T_k = \frac{L_k}{v^{(k)}/A^{(k)}}$$

is the total holding time of the kth reactor, k = 1, 2.

According to equations (7) and (8), the Hamiltonian function and the adjoint variable functions can be written as

$$H^{(1)} = -k_1^{(1)}x_1^{(1)}z_1^{(1)} + (k_1^{(1)}x_1^{(1)} - k_2^{(1)}x_2^{(1)})\, z_2^{(1)} \tag{29}$$

$$H^{(2)} = -k_1^{(2)}x_1^{(2)}z_1^{(2)} + (k_1^{(2)}x_1^{(2)} - k_2^{(2)}x_2^{(2)})\, z_2^{(2)} \tag{30}$$

$$H^{(3)} = 0 \tag{31}$$

$$\frac{dz_1^{(1)}}{dt} = k_1^{(1)}z_1^{(1)} - k_2^{(1)}z_2^{(1)} \tag{32}$$

$$\frac{dz_2^{(1)}}{dt} = k_2^{(1)}z_2^{(1)} \tag{33}$$

$$\frac{dz_1^{(2)}}{dt} = k_1^{(2)}z_1^{(2)} - k_2^{(2)}z_2^{(2)} \tag{34}$$

$$\frac{dz_2^{(2)}}{dt} = k_2^{(2)}z_2^{(2)} \tag{35}$$

$$\frac{dz_1^{(3)}}{dt} = \frac{dz_2^{(3)}}{dt} = 0 \tag{36}$$

According to equation (9), the adjoint variables at the separating point are given by

$$\begin{aligned} z_1^{(1)}(T_1) &= z_1^{(2)}(0) + z_1^{(3)}(0) \\ z_2^{(1)}(T_1) &= z_2^{(2)}(0) + z_2^{(3)}(0) \end{aligned} \tag{37}$$

Since it is desired to maximize the intermediate product B at the ends of branches 2 and 3, the objective function is

$$S = x_2^{(2)}(T_2) + x_2^{(3)}(T_3)$$

Consequently

$$c_2^{(2)} = c_2^{(3)} = 1 \tag{38}$$

$$c_1^{(2)} = c_1^{(3)} = 0 \tag{39}$$

Substitution of equations (38) and (39) into equation (11) yields at the final points

$$z_1^{(2)}(T_2) = z_1^{(3)}(T_3) = 0 \tag{40}$$

$$z_2^{(2)}(T_2) = z_2^{(3)}(T_3) = -1 \tag{41}$$

The optimal temperature, $\bar{\theta}(t)$, is determined from the condition that H is minimum at every point of each branch. Assuming that the minimum of H occurs at the stationary point, the optimal decision for branch 1 can be obtained from

$$\frac{\partial H^{(1)}}{\partial \theta^{(1)}} = - x_1^{(1)} z_1^{(1)} \frac{dk_1^{(1)}}{d\theta^{(1)}} + \left(\frac{dk_1^{(1)}}{d\theta^{(1)}} x_1^{(1)} - \frac{dk_2^{(1)}}{d\theta^{(1)}} x_2^{(1)}\right) z_2^{(1)} = 0$$

or

$$\begin{aligned}(z_2^{(1)} x_1^{(1)} - z_1^{(1)} x_1^{(1)})\, k_{10} E_1 \exp\,(-E_1/R\theta^{(1)}) \\ - z_2^{(1)} x_2^{(1)}\, k_{20} E_2 \exp\,(-E_2/R\theta^{(1)}) = 0\end{aligned} \tag{42}$$

Solution of this equation for $\theta^{(1)}$ gives

$$\bar{\theta}^{(1)}(t) = \left(\frac{E_1 - E_2}{R}\right) \frac{1}{\ln \left\lfloor \xi \dfrac{x_1^{(1)}(z_2^{(1)} - z_1^{(1)})}{x_2^{(1)} z_2^{(1)}} \right\rfloor} \tag{43}$$

where

$$\xi = \frac{k_{10} E_1}{k_{20} E_2}$$

Similarly, for branch 2, one obtains

$$\bar{\theta}^{(2)}(t) = \left(\frac{E_1 - E_2}{R}\right) \frac{1}{\ln \left\lfloor \xi \dfrac{x_1^{(2)}(z_2^{(2)} - z_1^{(2)})}{x_2^{(2)} z_2^{(2)}} \right\rfloor} \tag{44}$$

Substitution of equation (43) into equations (20), (21), (32), and (33), and equation (44) into equations (22), (23), (34), and (35) yields

$$\frac{dx_1^{(1)}}{dt} = - k_{10} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_1} x_1^{(1)} \tag{45}$$

$$\begin{aligned} \frac{dx_2^{(1)}}{dt} = {} & k_{10} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_1} x_1^{(1)} \\ & - k_{20} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_2} x_2^{(1)} \end{aligned} \tag{46}$$

$$\frac{dz_1^{(1)}}{dt} = k_{10} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_1} (z_1^{(1)} - z_2^{(1)}) \tag{47}$$

$$\frac{dz_2^{(1)}}{dt} = k_{20} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_2} z_2^{(1)} \tag{48}$$

$$\frac{dx_1^{(2)}}{dt} = - k_{10} \left\lfloor \xi \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_1} x_1^{(2)} \tag{49}$$

$$\begin{aligned} \frac{dx_2^{(2)}}{dt} = {} & k_{10} \left\lfloor \xi \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_1} x_1^{(2)} \\ & - k_{20} \left\lfloor \xi \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_2} x_2^{(2)} \end{aligned} \tag{50}$$

$$\frac{dz_1^{(2)}}{dt} = k_{10} \left\lfloor \xi \, \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_1} (z_1^{(2)} - z_2^{(2)}) \qquad (51)$$

$$\frac{dz_2^{(2)}}{dt} = k_{20} \left\lfloor \xi \, \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_2} z_2^{(2)} \qquad (52)$$

where

$$\lambda_1 = \frac{E_1}{E_2 - E_1} \qquad\qquad \lambda_2 = \frac{E_2}{E_2 - E_1}$$

For this system of eight differential equations, eight boundary conditions are needed, which can be summarized as follows:

$$x_1^{(1)}(0) = \alpha_1 \qquad (20)$$

$$x_2^{(1)}(0) = \alpha_2 \qquad (21)$$

$$x_1^{(1)}(T_1) = x_1^{(2)}(0) \qquad (25)$$

$$x_2^{(1)}(T_1) = x_2^{(2)}(0) \qquad (26)$$

$$z_1^{(2)}(T_2) = 0 \qquad (40)$$

$$z_2^{(2)}(T_2) = -1 \qquad (41)$$

$$z_1^{(1)}(T_1) = z_1^{(2)}(0) \qquad (53)$$

$$z_2^{(1)}(T_1) = z_2^{(2)}(0) - 1 \qquad (54)$$

Equations (53) and (54) are obtained by combining equations (36), (40), and (41) with equation (37).

The numerical calculations for the system described by equations (45) through (52) are illustrated with the use of the following data:

$k_{10} = 0.535 \times 10^{11}$ (minute)$^{-1}$

$k_{20} = 0.461 \times 10^{18}$ (minute)$^{-1}$

E_1 = 18,000 cal/mole

E_2 = 30,000 cal/mole

R = 2 cal/mole °K

T_1 = 10 minute

T_2 = 8 minute

α_1 = 0.72 moles/liter

α_2 = 0.24 moles/liter

An approximate iterative Runge-Kutta method was used together with a backward integration procedure to obtain the numerical results. The numerical procedure is as follows:

1. Differentiate equation (45) with respect to $x_1^{(1)}(T_1)$, equation (46) with respect to $x_2^{(1)}(T_1)$, equation (49) with respect to $x_1^{(2)}(T_2)$, and equation (50) with respect to $x_2^{(2)}(T_2)$ to obtain four additional first order differential equations. They are:

$$\frac{dG_1^{(1)}}{dt} = \frac{d\left(\frac{dx_1^{(1)}}{dt}\right)}{dx_1^{(1)}(T_1)} = - k_{10} (\lambda_1 + 1) \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right)\right\rfloor^{\lambda_1} G_1^{(1)} \quad (54a)$$

$$\frac{dG_2^{(1)}}{dt} = \frac{d\left(\frac{dx_2^{(1)}}{dt}\right)}{dx_2^{(1)}(T_1)} = - k_{10}\lambda_1 \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right)\right\rfloor^{\lambda_1} \left(\frac{x_1^{(1)}}{x_2^{(1)}}\right) G_2^{(1)}$$

$$+ k_{20} (\lambda_2 - 1) \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right)\right\rfloor^{\lambda_2} G_2^{(1)} \quad (54b)$$

$$\frac{dG_1^{(2)}}{dt} = \frac{d\left(\frac{dx_1^{(2)}}{dt}\right)}{dx_1^{(2)}(T_2)} = - k_{10} \; (\lambda_1 + 1) \left\lfloor \xi \; \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_1} G_1^{(2)} \qquad (54c)$$

$$\frac{dG_2^{(2)}}{dt} = \frac{d\left(\frac{dx_2^{(2)}}{dt}\right)}{dx_2^{(2)}(T_2)} = - k_{10} \; \lambda_1 \left\lfloor \xi \; \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_1} \left(\frac{x_1^{(2)}}{x_2^{(2)}}\right) G_2^{(2)}$$

$$+ \; k_{20} \; (\lambda_2 - 1) \left\lfloor \xi \; \frac{x_1^{(2)}}{x_2^{(2)}} \left(\frac{z_2^{(2)} - z_1^{(2)}}{z_2^{(2)}}\right) \right\rfloor^{\lambda_2} G_2^{(2)} \qquad (54d)$$

where

$$G_1^{(1)} = \frac{dx_1^{(1)}}{dx_1^{(1)}(T_1)}, \qquad G_2^{(1)} = \frac{dx_2^{(1)}}{dx_2^{(1)}(T_1)}$$

$$G_1^{(2)} = \frac{dx_1^{(2)}}{dx_1^{(2)}(T_2)}, \qquad G_2^{(2)} = \frac{dx_2^{(2)}}{dx_2^{(2)}(T_2)} \qquad (54e)$$

The boundary conditions for $G_1^{(1)}$, $G_2^{(1)}$, $G_1^{(2)}$, and $G_2^{(2)}$ are

$$G_1^{(1)}(T_1) = \left. \frac{dx_1^{(1)}}{dx_1^{(1)}(T_1)} \right|_{t=T_1} = 1, \quad G_2^{(1)}(T_1) = \left. \frac{dx_2^{(1)}}{dx_2^{(1)}(T_1)} \right|_{t=T_1} = 1$$

$$G_1^{(2)}(T_2) = \left. \frac{dx_1^{(2)}}{dx_1^{(2)}(T_2)} \right|_{t=T_2} = 1, \quad G_2^{(2)}(T_2) = \left. \frac{dx_2^{(2)}}{dx_2^{(2)}(T_2)} \right|_{t=T_2} = 1 \qquad (54f)$$

Thus, for these four additional equations, equations (54a) through (54d), one has four additional boundary conditions, equation (54f). In the derivation of these equations, equations (54a) through (54d), the assumption that only $x_1^{(1)}$ is a function of $x_1^{(1)}(T_1)$, only $x_2^{(1)}$ is a function of $x_2^{(1)}(T_1)$, only $x_1^{(2)}$ is a function of $x_1^{(2)}(T_2)$, and only $x_2^{(2)}$ is a function of $x_2^{(2)}(T_2)$ is made.

2. Assume values for $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$. Note that

$$z_1^{(2)}(T_2) = 0 , \qquad z_2^{(2)}(T_2) = -1$$

and

$$G_1^{(2)}(T_2) = 1 , \qquad G_2^{(2)}(T_2) = 1$$

3. Use the fourth-order Runge-Kutta method integrating backward equations (49) through (52), equations (54c) and (54d) to obtain $x_1^{(2)}(0)$, $x_2^{(2)}(0)$, $z_1^{(2)}(0)$, $z_2^{(2)}(0)$, $G_1^{(2)}(0)$, and $G_2^{(2)}(0)$.

4. Obtain $x_1^{(1)}(T_1)$, $x_2^{(1)}(T_1)$, $z_1^{(1)}(T_1)$, and $z_2^{(1)}(T_1)$ from equations (25), (26), (52), and (53) respectively. Note that

$$G_1^{(1)}(T_1) = 1 \qquad \text{and} \qquad G_2^{(1)}(T_1) = 1$$

5. Integrate backward employing the fourth-order Runge-Kutta method to obtain $x_1^{(1)}(0)$, $x_2^{(1)}(0)$, $z_1^{(1)}(0)$, $z_2^{(1)}(0)$, $G_1^{(1)}(0)$, and $G_2^{(1)}(0)$.

6. Use the derivative approximations

$$G_1^{(1)}(0) = \left.\frac{dx_1^{(1)}}{dx_1^{(1)}(T_1)}\right|_{t=0} \approx \frac{x_1^{(1)}(0) - \alpha_1}{x_1^{(1)}(T_1) - \xi_1^{(1)}}$$

$$G_2^{(1)}(0) = \left.\frac{dx_2^{(1)}}{dx_2^{(1)}(T_1)}\right|_{t=0} \approx \frac{x_2^{(1)}(0) - \alpha_2}{x_2^{(1)}(T_1) - \xi_2^{(1)}}$$

to compute $\xi_1^{(1)}$ and $\xi_2^{(1)}$ which are better approximations to the values of $x_1^{(1)}(T_1)$ and $x_2^{(1)}(T_1)$ than those obtained in Step 4.

7. Obtain from equations (25) and (27) closer approximations to the correct values of $x_1^{(2)}(0)$ and $x_2^{(2)}(0)$. Let these values be $\xi_1^{(1)}$ and $\xi_2^{(1)}$ (These values are identical with those obtained in Step 6).

8. Use the modified derivative approximations

$$G_1^{(2)}(0) = \frac{dx_1^{(2)}}{dx_1^{(2)}(T_2)}\Bigg|_{t\,=\,0} \approx \frac{\frac{1}{2}(x_1^{(2)}(0) - \xi_1^{(1)})}{x_1^{(2)}(T_2) - \xi_1^{(2)}}$$

$$G_2^{(2)}(0) = \frac{dx_2^{(2)}}{dx_2^{(2)}(T_2)}\Bigg|_{t\,=\,0} \approx \frac{\frac{1}{2}(x_2^{(2)}(0) - \xi_2^{(1)})}{x_2^{(2)}(T_2) - \xi_2^{(2)}}$$

to obtain $\xi_1^{(2)}$ and $\xi_2^{(2)}$, which are the new trial values for $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$.

9. Repeat steps 3 through 8 by using the new trial values until the computed values of $x_1^{(1)}(0)$ and $x_2^{(1)}(0)$ are approximately equal to α_1 and α_2 respectively.

10. Calculate the optimal decisions $\bar{\theta}^{(1)}(t)$ and $\bar{\theta}^{(2)}(t)$ according to equations (43) and (44).

This computational procedure was programmed for an IBM 1620. The main difficulty of the computation is the guess of the first assumed values for $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$. Because meaningless results would be obtained if either x_1, x_2, or $(z_2-z_1)/z_2$ became negative in any branch, and a very long time would be needed to obtain convergence to the desired values if the guess was too far away from the correct values, a careful choice of the value of $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$ was necessary. To do that, a table of optimal solutions without any iteration was obtained first. This was done as follows:

Arbitrarily but reasonably pick sets of $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$. For each set of $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$ together with given values of $z_1^{(2)}(T_2)$ and $z_2^{(2)}(T_2)$ employ the fourth-order Runge-Kutta method and backward integration to integrate equations (45) through (52) to obtain a set of values of $x_1^{(1)}(0)$ and $x_2^{(1)}(0)$. Each backward integration gives the optimal path corresponding to the initial conditions thus computed.

Integrating in this way for many sets of $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$, an optimal solution table is obtained. It is worthwhile to mention here that a slight change of either $x_1^{(2)}(T_2)$ or $x_2^{(2)}(T_2)$ would result in a large change in $x_1^{(1)}(0)$ and $x_2^{(1)}(0)$.

By investigating the above mentioned table and noting the initial conditions, $x_1^{(1)}(0)$ and $x_2^{(2)}(0)$, the values of $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$ for the iteration calculation were chosen. Even though $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$ were selected in this manner, the convergence of the calculation still was such that the answer could not be obtained in a reasonable period of time. To overcome this difficulty, a modified derivative approximation for the values of $G_1^{(2)}(0)$ and $G_2^{(2)}(0)$, which is given in Step 8 of the numerical procedures, was used. The reason that this modification was needed might be due to the fact that there are junction equations relating the end values of the state variables and adjoint variables of branch 1 with the initial values of branch two. In each trial calculation, new trial values of $x_1^{(2)}(T_2)$ and $x_2^{(2)}(T_2)$ were obtained by the equations in Step 8, which involve the state variables of both branches. It could be because of this "sudden jump" or "smoothlessness" which made the convergence difficult to obtain. By employing the modified derivative approximations, about six minutes of computer time was consumed for each trial calculation. The rate of convergence became slower as the computed values of $x_1^{(1)}(0)$ and $x_2^{(2)}(0)$ converged toward the given initial conditions. During the calculation new trial values can also be put in to make convergence faster by observing the trends of the results coming out. The results of computation are presented in dimensionless time, that is

$$\eta_1 = \frac{t}{T_1}$$

as shown in Table 1 and Figures 4 and 5. For the first assumed values, $x_1^{(2)}(T_2) = 0.115$, $x_2^{(2)}(T_2) = 0.72$, the computer took about two hours to obtain the solution shown in Table 1.

Figure 5 shows that the optimal temperature for reactor 2 is almost constant along the reactor. For design purposes, this indicates that isothermal operation in the second reactor will almost meet the optimum conditions. Even though this fact depends on the specific numerical data chosen and might not always be true, one still can safely assume that the optimal temperature profile in the second reactor for this kind of system will probably always be flatter than that of the first one.

It should also be noted that the geometry of the reactor arrangement in this system is equivalent to one plug flow reactor of total holding time $T = T_1 + T_2$, with a side exit stream at $t = T_1$. The system has the characteristics of a plug-flow reactor, provided that the product concentration from the exit stream is not to be maximized. If, as in this problem, the linear combination of end product concentrations from branches 2 and 3 is to be maximized, such an equivalence no longer exists. This fact can be visualized from the boundary conditions given in equations (41) and (54). If only the end product concentration from branch 2 is to be maximized, the condition in equation (41) should be changed to $z_2^{(3)}(T_3) = 0$, which combines with equation (37) to give $z_2^{(1)}(T_1) = z_2^{(2)}(0)$ rather than the value given in equation (54). This changes the problem from that of a simple exit, because both the optimal concentration and temperature are affected by the values of the adjoint variables.

b. Two Tubular Flow Reactors in Series with Intermediate Fresh Feed

Table 1. Computational results for the reaction A→B→C taking place in two tubular reactors in series with intermediate product withdrawal.

	$x_1^{(2)}$	$x_2^{(2)}$	$z_1^{(2)}$	$z_2^{(2)}$	$\theta^{(2)}$
1.0	0.11315	0.70630	0.00000	-1.00000	327.66
0.9	0.11901	0.70387	-0.04917	-0.99515	327.72
0.8	0.12522	0.70111	-0.09591	-0.99027	327.79
0.7	0.13178	0.69801	-0.14033	-0.98538	327.85
0.6	0.13873	0.69455	-0.18253	-0.98046	327.93
0.5	0.14609	0.69069	-0.22261	-0.97552	328.00
0.4	0.15389	0.68640	-0.26067	-0.97055	328.08
0.3	0.16217	0.68166	-0.29679	-0.96555	328.17
0.2	0.17097	0.67642	-0.33105	-0.96051	328.26
0.1	0.18031	0.67064	-0.36355	-0.95542	328.36
0.0	0.19026	0.66429	-0.39436	-0.95030	328.47

	$x_1^{(1)}$	$x_2^{(1)}$	$z_1^{(1)}$	$z_2^{(1)}$	$\theta^{(1)}$
1.0	0.19026	0.66429	-0.39436	-1.95030	334.15
0.9	0.21205	0.65235	-0.55271	-1.92134	334.39
0.8	0.23688	0.63752	-0.69462	-1.89178	334.68
0.7	0.26538	0.61919	-0.82149	-1.86144	335.02
0.6	0.29831	0.59658	-0.93455	-1.83009	335.42
0.5	0.33678	0.56863	-1.03493	-1.79738	335.92
0.4	0.38229	0.53383	-1.12361	-1.76282	336.54
0.3	0.43717	0.48988	-1.20146	-1.72561	337.35
0.2	0.50520	0.43303	-1.26921	-1.68435	338.48
0.1	0.59363	0.35607	-1.32739	-1.63616	340.20
0.0	0.72084	0.24071	-1.37616	-1.57259	343.58

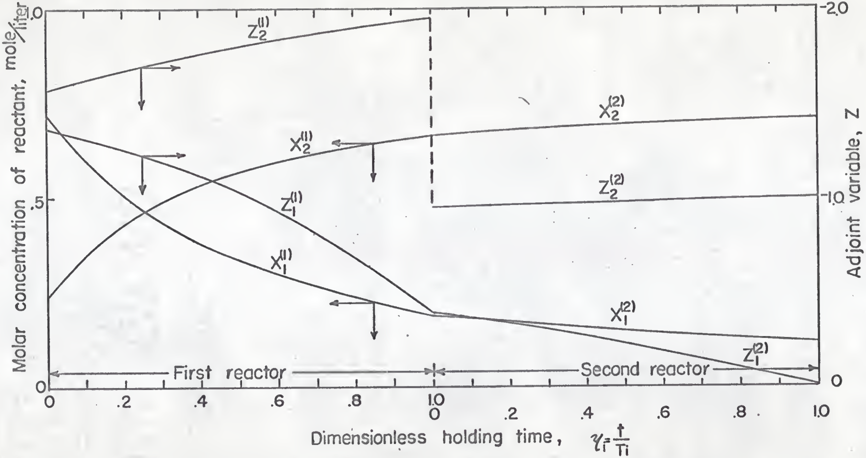

Fig.4 Optimal concentration profiles in two tubular reactors connected in series with product withdrawn from the intermediate point for the reaction A→B→C.

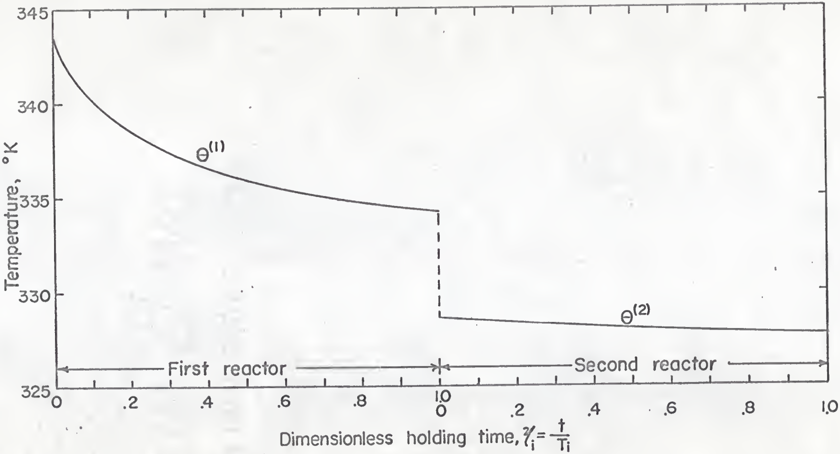

Fig. 5 Optimal temperature profiles in two tubular reactors connected in series with product withdrawn from the intermediate point for the reaction A→B→C.

In Section a, a continuous complex process involving a separating point has been discussed. In this section, a similar problem will be considered, i.e. a reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ is taking place in the reactors, but the geometrical arrangement involves a combining point rather than a separating point. A schematic diagram for this process is shown in Figure 6. In this figure, $v^{(k)}$ represents the volumetric flow rate through the kth branch. It is seen that the reactor arrangement is similar to that of Section a, except an additional fresh feed streams is introduced at an intermediate point of the two reactors rather than a withdrawal of side stream product. The lengths of the reactors, L_1 and L_3 and the cross-sectional areas $A^{(1)}$ and $A^{(3)}$ are all preassigned, that is, the volumes of the reactors are fixed. In this study, $v^{(1)}$ and $v^{(3)}$, the volumetric through-put to the first reactor (branch 1) and the second reactor (branch 3) respectively, are fixed, i.e., the total holding time in both reactors has been specified. It is desired to maximize the intermediate product B at the end of the second reactor by proper choice of temperature along the two two tubular reactors with given inlet concentrations of both feed streams. The flows in the reactors are again assumed to be of the plug flow type.

From the material balance of each component, as carried out in Section a, the performance equations for branches 1 and 3 where the reactions take place can be written as

$$\frac{dx_1^{(1)}}{dt} = - k_1^{(1)} x_1^{(1)} \tag{55}$$

$$\frac{dx_2^{(1)}}{dt} = k_1^{(1)} x_1^{(1)} - k_2^{(1)} x_2^{(1)} \tag{56}$$

$$\frac{dx_1^{(3)}}{dt} = - k_1^{(3)} x_1^{(3)} \tag{57}$$

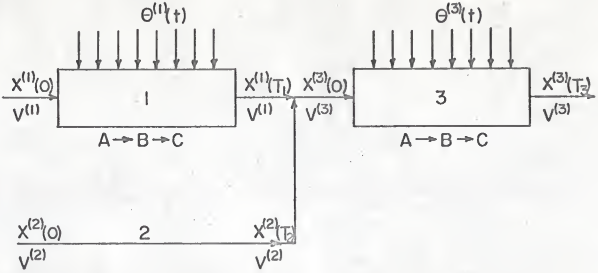

Fig. 6 Schematic diagram of two tubular reactors, connected in series with additional fresh feed fed into the intermediate point for the reaction $A \rightarrow B \rightarrow C$.

$$\frac{dx_2^{(3)}}{dt} = k_1^{(3)}x_1^{(3)} - k_2^{(3)}x_2^{(3)} \tag{58}$$

with the given initial concentration of A and B as $x_1^{(1)}(0) = \alpha_1$, $x_2^{(1)}(0) = \alpha_2$ respectively; x_1, x_2, t, k_1 and k_2 are the same as defined in Section a. Since there are no transformations taking place and no control actions imposed in branch 2, the performance equation for branch 2 is

$$\frac{dx_1^{(2)}}{dt} = \frac{dx_2^{(2)}}{dt} = 0 , \qquad \begin{array}{l} x_1^{(2)}(0) = \beta_1 \\ x_2^{(2)}(0) = \beta_2 \end{array} \tag{59}$$

where β_1 and β_2 are the concentrations of A and B respectively in the intermediate feed and are generally different from the values of α_1 and α_2. The junction equations at the combining point are derived based on the principle of conservation of mass. The application of this principle (the material balance) at the combining point yields

$$v^{(3)}x_1^{(3)}(0) = v^{(1)}x_1^{(1)}(T_1) + v^{(2)}x_1^{(2)}(T_2) \tag{60}$$

where $v^{(k)}$, k = 1, 2, 3 is the volumetric flow rate through the kth branch. If we let $\gamma_1 = v^{(1)}/v^{(3)}$ and $\gamma_2 = v^{(2)}/v^{(3)}$, equation (60) can be rewritten as

$$x_1^{(3)}(0) = \gamma_1 x_1^{(1)}(T_1) + \gamma_2 x_1^{(2)}(T_2) \tag{61}$$

According to equation (59) the concentrations of reactants 1 and 2 (A and B) remain constant along branch 2. It can, therefore, be replaced by a more general form as

$$x_1^{(2)}(0) = x_1^{(2)}(t) = x_1^{(2)}(T_2) = \beta_1 \tag{62}$$

Substituting equation (62) into equation (61) yields a junction equation at the combining point for reactant 1 as

$$x_1^{(3)}(0) = \gamma_1 x_1^{(1)}(T_1) + \gamma_2 \beta_1 \tag{63}$$

Similarly, for reactant 2 one obtains

$$x_2^{(3)}(0) = \gamma_1 x_2^{(1)}(T_1) + \gamma_2 \beta_2 \tag{64}$$

The initial states are

$$\begin{aligned} x_1^{(1)}(0) &= \alpha_1 \\ x_2^{(1)}(0) &= \alpha_2 \end{aligned} \tag{65}$$

According to equations (7) and (8), the Hamiltonian functions and the adjoint variable functions can be written as

$$H^{(1)} = z_1^{(1)}(-k_1^{(1)}x_1^{(1)}) + z_2^{(1)}(k_1^{(1)}x_1^{(1)} - k_2^{(1)}x_2^{(1)}) \tag{66}$$

$$H^{(2)} = 0 \tag{67}$$

$$H^{(3)} = z_1^{(3)}(-k_1^{(3)}x_1^{(3)}) + z_2^{(3)}(k_1^{(3)}x_1^{(3)} - k_2^{(3)}x_2^{(3)}) \tag{68}$$

$$\frac{dz_1^{(1)}}{dt} = k_1^{(1)}z_1^{(1)} - k_2^{(1)}z_2^{(1)} \tag{69}$$

$$\frac{dz_2^{(1)}}{dt} = k_2^{(1)}z_2^{(1)} \tag{70}$$

$$\frac{dz_1^{(2)}}{dt} = \frac{dz_2^{(2)}}{dt} = 0 \tag{71}$$

$$\frac{dz_1^{(3)}}{dt} = k_1^{(3)}z_1^{(3)} - k_2^{(3)}z_2^{(3)} \tag{72}$$

$$\frac{dz_2^{(3)}}{dt} = k_2^{(3)}z_2^{(3)} \tag{73}$$

According to equations (10), (63), and (64), one has at the combining point

$$z_1^{(1)}(T_1) = \gamma_1 z_1^{(3)}(0) \tag{74}$$

$$z_2^{(1)}(T_1) = \gamma_1 z_2^{(3)}(0) \tag{75}$$

Since the problem is to maximize the concentration of product B at the outlet of branch 3, the objective function is $x_2^{(3)}(T_3)$. Consequently $c_1^{(3)} = 0$ and $c_2^{(3)} = 1$. Thus, according to equation (11), one has at the final point

$$z_1^{(3)}(T_3) = 0 \tag{76}$$

$$z_2^{(3)}(T_3) = -1 \tag{77}$$

The optimal temperature, $\bar{\theta}(t)$, is determined in the same manner as is given in Section a. The result is

$$\bar{\theta}^{(k)}(t) = \left(\frac{E_1 - E_2}{R}\right) \frac{1}{\ln \left\lfloor \xi \dfrac{x_1^{(k)}(z_2^{(k)} - z_1^{(k)})}{x_2^{(k)} z_2^{(k)}} \right\rfloor} \tag{78}$$

where

$$k = 1,\ 3 \quad \text{and} \quad \xi = \frac{k_{10}E_1}{k_{20}E_2}$$

If this result is substituted into equations (55) through (58) and equations (69) through (73), one obtains

$$\frac{dx_1^{(1)}}{dt} = -k_{10} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_1} x_1^{(1)} \tag{79}$$

$$\frac{dx_2^{(1)}}{dt} = k_{10} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_1} x_1^{(1)}$$

$$- k_{20} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right) \right\rfloor^{\lambda_2} x_2^{(1)} \tag{80}$$

$$\frac{dx_1^{(3)}}{dt} = -k_{10} \left\lfloor \xi \frac{x_1^{(3)}}{x_2^{(3)}} \left(\frac{z_2^{(3)} - z_1^{(3)}}{z_2^{(3)}}\right)\right\rfloor^{\lambda_1} x_1^{(3)} \tag{81}$$

$$\begin{aligned}\frac{dx_2^{(3)}}{dt} = {} & k_{10} \left\lfloor \xi \frac{x_1^{(3)}}{x_2^{(3)}} \left(\frac{z_2^{(3)} - z_1^{(3)}}{z_2^{(3)}}\right)\right\rfloor^{\lambda_1} x_1^{(3)} \\ & - k_{20} \left\lfloor \xi \frac{x_1^{(3)}}{x_2^{(3)}} \left(\frac{z_2^{(3)} - z_1^{(3)}}{z_2^{(3)}}\right)\right\rfloor^{\lambda_2} x_2^{(3)}\end{aligned} \tag{82}$$

$$\frac{dz_1^{(1)}}{dt} = k_{10} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right)\right\rfloor^{\lambda_1} (z_1^{(1)} - z_2^{(1)}) \tag{83}$$

$$\frac{dz_2^{(1)}}{dt} = k_{20} \left\lfloor \xi \frac{x_1^{(1)}}{x_2^{(1)}} \left(\frac{z_2^{(1)} - z_1^{(1)}}{z_2^{(1)}}\right)\right\rfloor^{\lambda_2} z_2^{(1)} \tag{84}$$

$$\frac{dz_1^{(3)}}{dt} = k_{10} \left\lfloor \xi \frac{x_1^{(3)}}{x_2^{(3)}} \left(\frac{z_2^{(3)} - z_1^{(3)}}{z_2^{(3)}}\right)\right\rfloor^{\lambda_1} (z_1^{(3)} - z_2^{(3)}) \tag{85}$$

$$\frac{dz_2^{(3)}}{dt} = k_{20} \left\lfloor \xi \frac{x_1^{(3)}}{x_2^{(3)}} \left(\frac{z_2^{(3)} - z_1^{(3)}}{z_2^{(3)}}\right)\right\rfloor^{\lambda_2} z_2^{(3)} \tag{86}$$

To solve this system of eight differential equations, one needs eight boundary conditions which are given by equations (63), (64), and (65) and equations (74) through (77) and are summarized as follows:

$$x_1^{(3)}(0) = \gamma_1 x_1^{(1)}(T_1) + \gamma_2 \beta_1 \tag{63}$$

$$x_2^{(3)}(0) = \gamma_1 x_2^{(1)}(T_1) + \gamma_2 \beta_2 \tag{64}$$

$$\begin{aligned} x_1^{(1)}(0) &= \alpha_1 \\ x_2^{(1)}(0) &= \alpha_2 \end{aligned} \tag{65}$$

$$z_1^{(1)}(T_1) = \gamma_1 z_1^{(3)}(0) \tag{74}$$

$$z_2^{(1)}(T_1) = \gamma_1 z_2^{(3)}(0) \tag{75}$$

$$z_1^{(3)}(T_3) = 0 \tag{76}$$

$$z_2^{(3)}(T_3) = -1 \tag{77}$$

The numerical calculations for the system described by equations (78) through (86) are illustrated by using the following data:

$k_{10} = 0.535 \times 10^{11}$ minute^{-1}

$k_{20} = 0.461 \times 10^{18}$ minute^{-1}

$E_1 = 18{,}000$ cal/mole

$E_2 = 30{,}000$ cal/mole

$R = 2$ cal/mole $^{\circ}$K

$T_1 = 8$ minute

$T_3 = 10$ minute

$\alpha_1 = 0.72$ moles/liter

$\alpha_2 = 0.24$ moles/liter

$\beta_1 = 0.7$ moles/liter

$\beta_2 = 0.25$ moles/liter

An approximate iterative Runge-Kutta method together with a backward integration procedure was used to obtain the numerical solutions. The numerical procedures are similar to those used in Section a, except that in obtaining $x_1^{(1)}(T_1)$, $x_2^{(1)}(T_1)$, $z_1^{(1)}(T_1)$, and $z_2^{(1)}(T_1)$ one has to use the boundary conditions, equations (63), (64), (74) and (75) respectively (see Step 4 of Section a). These boundary conditions render the computation much more difficult. As one can see, equations (63) and (64) give

$$x_1^{(1)}(T_1) = \frac{1}{\gamma_1}\,(x_1^{(3)}(0) - \gamma_2\beta_1) \quad , \tag{87}$$

$$x_2^{(1)}(T_1) = \frac{1}{\gamma_1}\,(x_2^{(3)}(0) - \gamma_2\beta_2) \quad , \tag{88}$$

rather than

$$x_1^{(1)}(T_1) = x_1^{(2)}(0) \tag{25}$$

$$x_2^{(1)}(T_1) = x_2^{(2)}(0) \tag{27}$$

A slight change in $x_1^{(3)}(T_3)$ and $x_2^{(3)}(T_3)$ would greatly affect $x_1^{(1)}(T_1)$ and $x_2^{(1)}(T_1)$ which were responsible for the later calculations for branch 1. Meaningless results might result due to the appearance of negative values of x_1, x_2, or $(z_2 - z_1)/z_2$. The most critical part of the calculation was when the computer proceeded from the calculation of branch 3 to branch 1. A more elaborate table of optimal solutions as mentioned in Section a was needed to make a suitable choice for the first assumed values of $x_1^{(3)}(T_3)$ and $x_2^{(3)}(T_3)$ for the final iteration calculation, which employed the approximate iterative Runge-Kutta method.

In obtaining the new trial values for $x_1^{(3)}(T_3)$ and $x_2^{(3)}(T_3)$ for the iteration calculation, it was necessary to modify Steps 6, 7, and 8 as follows: (note that one has branch 3 instead of branch 2 for representing the second reactor)

6' Use the derivative approximation

$$G_1^{(1)}(0) = \left.\frac{dx_1^{(1)}}{dx_1^{(1)}(T_1)}\right|_{t=0} \approx \frac{x_1^{(1)}(0) - \alpha_1}{x_1^{(1)}(T_1) - \xi_1^{(1)}}$$

$$G_2^{(1)}(0) = \frac{dx_2^{(1)}}{dx_2^{(1)}(T_1)}\Bigg|_{t=0} \approx \frac{x_2^{(1)}(0) - \alpha_2}{x_1^{(1)}(T_1) - \xi_2^{(1)}}$$

to compute $\xi_1^{(1)}$ and $\xi_2^{(1)}$ which are better approximations of the values of $x_1^{(1)}(T_1)$ and $x_2^{(1)}(T_1)$

7' Obtain from equations (63) and (64) closer approximations to the correct values of $x_1^{(3)}(0)$ and $x_2^{(3)}(0)$, i.e.,

$$\eta_1^{(3)} = \gamma_1\xi_1^{(1)} + \gamma_2\beta_1 \tag{89}$$

$$\eta_2^{(3)} = \gamma_1\xi_2^{(1)} + \gamma_2\beta_2 \tag{90}$$

8' Use the modified derivative approximations

$$G_1^{(3)}(0) = \frac{dx_1^{(3)}}{dx_1^{(3)}(T_3)}\Bigg|_{t=0} \approx \frac{\frac{1}{2}(x_1^{(3)}(0) - \eta_1^{(3)})}{x_1^{(3)}(T_3) - \xi_1^{(3)}}$$

$$G_2^{(3)}(0) = \frac{dx_2^{(3)}}{dx_2^{(3)}(T_3)}\Bigg|_{t=0} \approx \frac{\frac{1}{2}(x_2^{(3)}(0) - \eta_2^{(3)})}{x_2^{(3)}(T_3) - \xi_2^{(3)}}$$

to obtain $\xi_1^{(3)}$ and $\xi_2^{(3)}$, which are the new trial values for $x_1^{(3)}(T_3)$ and $x_2^{(3)}(T_3)$.

As can be seen, during the calculation there was another "sudden-jump" in Steps 7' and 8'. This might also be one of the reasons why the computation was so unstable and so slow to converge.

This computation was also programmed on an IBM 1620 computer. About seven minutes were consumed for each trial calculation. The effects of γ_2, the flow rate fraction of fresh feed stream have been investigated for several values of γ_2. The stability and convergence of the computation became worse as the value of γ_2 became greater. This is a result that one should expect from observation of the boundary conditions given in equations

(87) through (90).

It should be noted that in this study, the values of total holding time, T_1 and T_3 were fixed even though the fractional amount of fresh feed, γ_2, was varying. To make $T_1 = 8$ min. and $T_2 = 10$ min., either one can specify the volume of the second reactor, fix the flow rate, $v^{(3)}$, and adjust the size of the first reactor and the flow rate, $v^{(1)}$, or one can adjust the sizes of both reactors and choose the flow rates $v^{(1)}$ and $v^{(2)}$ according to various chosen values of γ_2. The results of the computation are shown in Figures 7 and 8. The optimal solution and the values of the adjoint variable function for the case $\gamma_2 = 0.5$ are also shown in Table 2 and Figure 9 for the purpose of illustration.

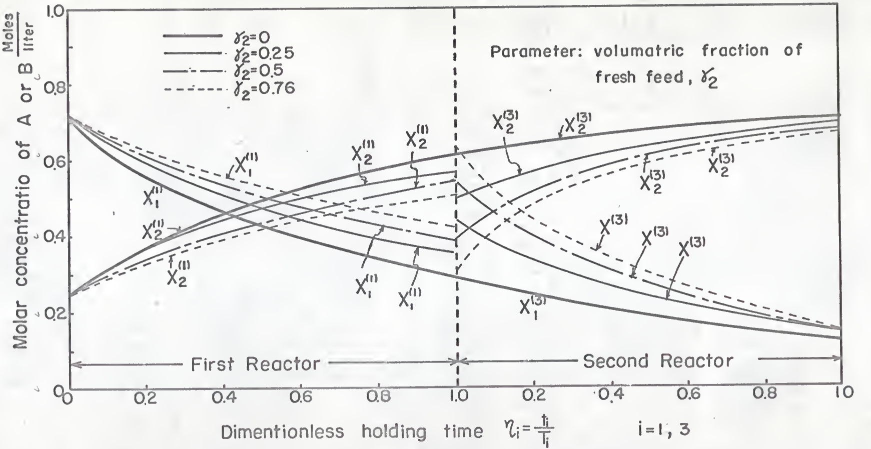

Fig. 7 Optimal concentration profiles in two tubular reactors connected in series with additional fresh feed fed into the intermediate point for the reaction A → B → C.

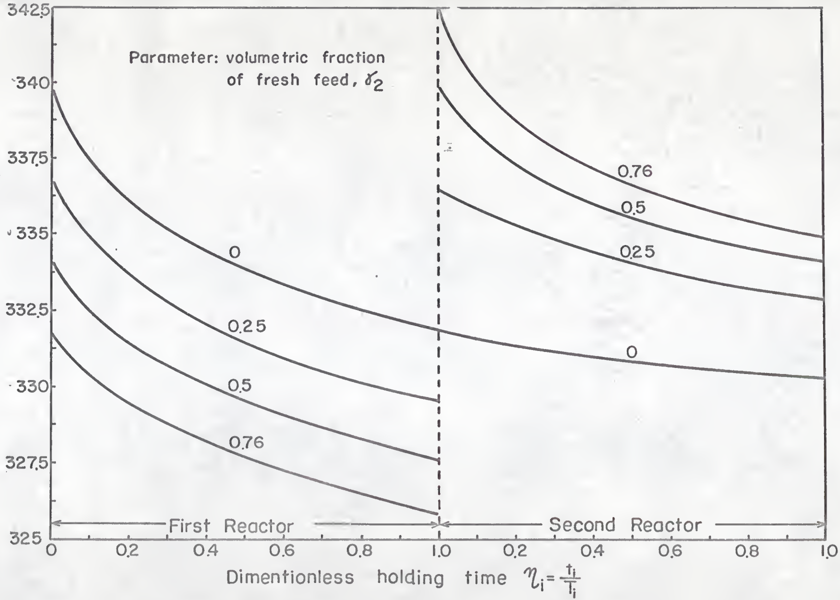

Fig. 8 Optimal temperature profiles in tubular reactors connected in series with additional fresh feed fed into the intermediate point for the reaction $A \rightarrow B \rightarrow C$.

Table 2. Computational results for the reaction $A \rightarrow B \rightarrow C$ taking place in two tubular reactors connected in series with intermediate feed for the case $\gamma_2 = 0.5$

η	$x_1^{(3)}$	$x_2^{(3)}$	$z_1^{(3)}$	$z_2^{(3)}$	$\theta^{(3)}$
1.0	0.15552	0.67714	0.00000	-1.00000	334.24
0.9	0.17344	0.66939	-0.10252	-0.98501	334.44
0.8	0.19378	0.65937	-0.19437	-0.96982	334.67
0.7	0.21700	0.64665	-0.27648	-0.95436	334.93
0.6	0.24364	0.63068	-0.34972	-0.93856	335.25
0.5	0.27442	0.61074	-0.41484	-0.92231	335.62
0.4	0.31033	0.58588	-0.47256	-0.90544	336.07
0.3	0.35270	0.55477	-0.52348	-0.88776	336.63
0.2	0.40351	0.51545	-0.56814	-0.86891	337.35
0.1	0.46590	0.46482	-0.60701	-0.84834	338.32
0.0	0.54543	0.39735	-0.64046	-0.82499	340.00

η	$x_1^{(1)}$	$x_2^{(1)}$	$z_1^{(1)}$	$z_2^{(1)}$	$\theta^{(1)}$
1.0	0.39084	0.54469	-0.32023	-0.41249	327.70
0.9	0.41136	0.52684	-0.32478	-0.41045	327.97
0.8	0.43349	0.50738	-0.32910	-0.40834	328.28
0.7	0.45747	0.48609	-0.33319	-0.40613	328.63
0.6	0.48360	0.46266	-0.33707	-0.40383	329.02
0.5	0.51225	0.43673	-0.34074	-0.40140	329.48
0.4	0.54392	0.40780	-0.34419	-0.39880	330.03
0.3	0.57930	0.37517	-0.34744	-0.39601	330.69
0.2	0.61942	0.33782	-0.35049	-0.39294	331.51
0.1	0.66589	0.29415	-0.35333	-0.38948	332.59
0.0	0.72160	0.24126	-0.35600	-0.38540	334.00

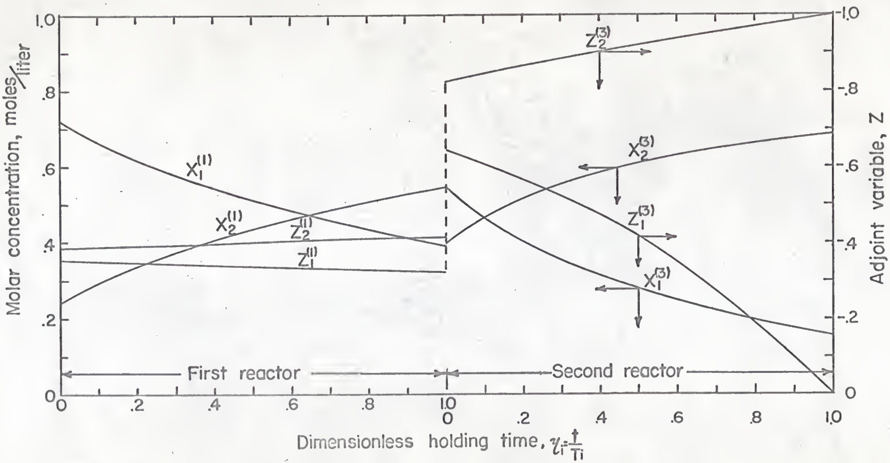

Fig. 9 Optimal concentration profiles in two tubular reactors connected in series with fresh feed fed into the intermediate point for the reaction A → B → C for the case $\tau_2 = 0.5$.

4. COMBINED USE OF THE MAXIMUM PRINCIPLE AND DYNAMIC PROGRAMMING

The best design job requires the "optimal" use of every tool available. Among many of the recently developed dynamic optimization techniques, dynamic programming and the maximum principle appear to be two of the most powerful for optimizing complex processes consisting of more than one process unit. Each of these methods, however, has comparative advantages over the other, depending upon the problem to be solved. By combining these two techniques, it is often possible to handle optimization of a complicated process with less effort.

a. A Comparison of the Maximum Principle and Dynamic Programming

The dynamic programming method reduces a complicated problem into a simple algorithm ideally suited for modern computers. It is based upon the principle of optimality and employs the technique of invariant imbedding [12]. Dynamic programming, however, has its limitations. Since one is imbedding a whole family of processes in order to obtain the solution of one particular process, dynamic programming is often an expensive proposition both in time and in space, and since both the computer time and the required memory increase rapidly with an increase in the number of state variables, this technique in general can be used successfully only for problems with small numbers of state variables. Even if one has a considerable amount of computer time, the available memory in most modern computers still limits the use of the dynamic programming technique to problems of not more than three or four state variables. It is not suited for solving continuous problems in which the application of dynamic programming leads to a set of partial differential equations. It is possible, of course, to convert this set of partial differential equations into a system of finite difference equations and apply the method of dynamic programming to solve continuous problems. The computational difficulty, however, will be even more pronounced in this case because a very small increment of finite difference equations must be taken in order to obtain a solution with reasonable accuracy.

Another disadvantage of dynamic programming is that it cannot be conveniently applied to processes in which the optimum conditions at any stage can be disturbed by conditions at the following stages. This is a fairly serious limitation if one considers the various countercurrent operations employed in the chemical and petroleum industries.

However, the definite and significant advantage of dynamic programming in the optimization of processes with constraints on state variables cannot be neglected. Processes with bounded state variables give no touble with this method, because the optimal decisions determined for the entire allowable policy domain automatically satisfy the constraints.

On the other hand, the maximum principle can be used to handle most constraints of ordinary optimum design problems with the exception of those in the state variables which cannot be handled routinely. By the use of the maximum principle the optimization problem is essentially reduced to a maximum- or minimum- seeking problem subject to a set of ordinary differential equations and certain inequality constraints. This set of ordinary differential equations usually forms a two-point boundary value problem. Thus one is still limited by the difficulties encountered in solving a set of simultaneous nonlinear differential equations with two-point boundary conditions. Nevertheless, the number of state variables that can be treated by usually available computing equipment when the maximum principle is used may be larger than that when the dynamic programming technique is used. Furthermore, the maximum principle is probably more suited for solving continuous problems than dynamic programming is.

Another salient feature of dynamic programming is that it can be used to handle processes for which the transformation at each stage is expressed in a form other than that of a mathematical equation (for example, a table or a graph). The maximum principle, on the other hand, is applicable only to processes with well-defined performance equations, and the transformation function must be continuously differentiable with respect to the state variables.

The combined use of the maximum principle and dynamic programming can be employed for the optimization of some complex processes. A process can be separated into different units, and each unit can be optimized by either of the two methods (or by any other appropriate optimization method). The overall process is then optimized by connecting the different units by use of the principle of optimality. This combination can be referred to as the sequential union of the maximum principle and dynamic programming.

On the other hand, since the maximum principle only gives the necessary conditions for local maximum (minimum), there is no assurance that the optimal policy found by the maximum principle is the global optimal policy. Since the method of dynamic programming employs the so-called imbedding technique which is, in its spirit, similar to the exhaustive search, the optimal policy obtained by dynamic programming will always be the global optimal policy provided that the interpolation error inherent to the method is small. It is thus proposed that, when an accurate solution is desired or required, the method of dynamic programming be employed first to locate the approximate position of the global maximum and that the maximum principle then be applied to pinpoint the maximum point. This combination may be called the parallel union of the maximum principle and dynamic programming.

In the following section the method of sequential union will be presented in detail.

b. Sequential Union of the Maximum Principle and Dynamic Programming

The essential steps in the application of the sequential union of the maximum principle and dynamic programming are summarized as follows [21]:

(1) An entire process is first divided into different units (subprocesses).

(2) An appropriate optimization method is applied to each unit.

(3) Then, the optimum of the entire process is obtained by the principle of optimality.

The separation of a process into different units is arbitrary, and is often dictated by a knowledge of the process and its requirements. For example, a chemical manufacturing process which requires a reactor, an extractor and a heat exchanger may be divided into three or more units. In the purification of a chemical compound from a mixture by several distillation columns, one can consider each distillation column as a unit, or one can consider all the distillation columns together as a single unit, depending on the optimization requirements and on the complexity and physical characteristics of the process.

Each unit may be composed of a number of stages, or it may just represent a continuous process. In a series of stirred tank reactors, each stirred tank may be considered as a stage. A tubular flow reactor may be considered as a continuous process consisting of an infinite number of stirred tanks.

A two-unit process will illustrate the method of sequential union. The arrangements of the units and the number of stages in each unit are shown in

Figure 10 in which Unit 1 is a continuous process and Unit 2 is a discrete process. It is assumed that the maximum principle is to be applied to Unit 1 and dynamic programming to Unit 2. The over all optimum is then obtained by applying the principle of optimality.

For the continuous simple process of Unit 1, one knows from Section 2a that the performance equations are generally given by

$$\frac{dx_i}{dt} = f(x_1, \ldots, x_s; \theta_1, \ldots, \theta_r) , \quad i = 1, 2, \ldots, s ,$$

or in vector form

$$\frac{dx}{dt} = f(x;\theta) \tag{91}$$

The aim is usually to optimize a linear combination of the final values of the state variables of this unit, that is, to maximize (or minimize) the quantity

$$S = \sum_{i=1}^{s} c_i x_i(T) \tag{92}$$

with the initial condition $x(t_0) = \alpha$ given. To do this, one generally introduces an s-dimensional adjoint vector $z(t)$ and a Hamiltonian function H which satisfy the following relations

$$H(z,x,t) = \sum_{i=1}^{s} z_i f_i(x;\theta) \tag{93}$$

$$\frac{dz_i}{dt} = - \frac{\partial H}{\partial x_i} , \qquad i = 1, 2, \ldots, s \tag{94}$$

and the boundary conditions

$$x(t_0) = \alpha , \quad z_i(T) = - c_i , \qquad i = 1, \ldots, s \tag{95}$$

The optimal solution is obtained only if the function H is minimized

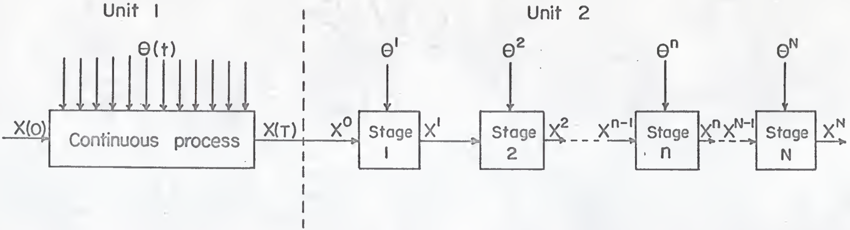

Fig.10A Schematic representation of a two-unit process.

(or maximized) at every moment $t = t_0$ to $t = T$, subject to equations (91), (94), and (95).

For the discrete process of Unit 2, the transformation of the process stream at the nth stage may be described by a set of difference equations [7]

$$x_i^n = f_i^n\,(x_1^{n-1}, x_2^{n-1}, \ldots, x_s^{n-1}; \theta_1^n, \theta_2^n, \ldots, \theta_r^n)^*, \quad i = 1, 2, \ldots, s$$

or in vector form

$$x^n = f^n\,(x^{n-1}; \theta^n) \tag{96}$$

which is the performance equation of this unit. Suppose that the return function (interval profit function) from stage n of Unit 2 is $h(x^{n-1}; \theta^n)$ and one wishes to maximize the total profit represented by

$$h(x^0; \theta^1) + h(x^1; \theta^2) + \ldots + h(x^{n-1}; \theta^n) + \ldots + h(x^{N-1}; \theta^N) \tag{97}$$

It should be noted that the value of this maximum depends only upon the initial state of the state variable and the number of stages. Thus, let

$$g_N(x^0) = \underset{\{\theta^n\}}{\mathrm{Max}} \left\lfloor h(x^0; \theta^1) + \ldots + h(x^{N-1}; \theta^N) \right\rfloor \tag{98}^{**}$$

Using the principle of optimality [12] and equation (96), one obtains a recurrence relation as

$$g_N(x^0) = \underset{\theta^1}{\mathrm{Max}} \left\{ h(x^0; \theta^1) + g_{N-1} \left\lfloor f(x^0; \theta^1) \right\rfloor \right\} \tag{99}$$

for $N = 2, 3, \ldots, N$. For $N = 1$, one has

---

* The superscript, n, indicates the stage number.

** Subscript N indicates the total number of stages but not the Nth stage.

$$g_1(x^0) = \underset{\theta^1}{\text{Max}}\, h(x^0;\, \theta^1) \tag{100}$$

Thus the optimization problem of Unit 2 can be solved recursively by using equations (99) and (100).

In order to obtain the over-all optimum for the process, the optimum of Unit 2 must be achieved first by the method of dynamic programming $\lfloor 12 \rfloor$. Since Unit 1 is to be optimized by the maximum principle, special attention must be given to the objective function for this unit. Because one has already obtained the optimum of Unit 2 by dynamic programming, equation (92) can be modified to include the effects of Unit 2. It should be noted that the optimum return for Unit 2 is in general given in tabular form. For every possible combination of the initial condition x^0, the value of the optimum return, g_N $\lfloor$see equation (99)$\rfloor$, is listed. In order to use the function $g_N(x^0)$ in establishing the return function for Unit 1, it must first be expressed in analytical form. This can be done sometimes by using appropriate correlation methods. For example, a polynomial approximation appears to be promising in these correlations. In a one-state variable process the $g_N(x^0)$ may be represented in an analytical form.

When the function $g_N(x^0)$ is expressed analytically, the objective function for the entire process can be obtained. If one lets $\int_0^T h(x;\, \theta)dt$ be the return (profit or cost) from Unit 1, the objective function for the over-all system is

$$S = g_N \lfloor x(T) \rfloor + \int_0^T h(x;\theta)dt \tag{101}$$

where $x(T) = x^0$, that is, $x(T)$ represents the final value of the state vector of Unit 1 and is equal to the initial value of the state vector of Unit 2.

Equation (101), which corresponds to the recurrence relation, equation (99), is established by the principle of optimality. The method outlined by equations (91) through (95), may now be modified to take into account the objective function, equation (101). To accomplish this, a new state variable is introduced as

$$x_{s+1}(T) = g_N \lfloor x(T) \rfloor + \int_0^T h(x;\theta)dt \tag{102}$$

or

$$x_{s+1}(t) = g_N \lfloor x(t) \rfloor + \int_0^t h(x;\theta)dt \tag{103}$$

and

$$\frac{dx_{s+1}}{dt} = \sum_{i=1}^{s} \frac{\partial g_N(x)}{\partial x_i} \frac{dx_i}{dt} + h(x;\theta) \tag{104}$$

The problem is now transformed into that of maximizing the final value of x_{s+1}. The Hamiltonian function H in equation (93) is modified as

$$H(x,z,\theta) = \sum_{i=1}^{s+1} z_i f_i(x;\theta) \tag{105}$$

and the new adjoint variable z_{s+1} is introduced as

$$\frac{dz_{s+1}}{dt} = - \frac{\partial H}{\partial x_{s+1}} = 0 \tag{106}$$

The boundary conditions for the adjoint variables, equation (105), should be changed to

$$\begin{aligned} &z_i(T) = 0 \;, \qquad i = 1, 2, \ldots, s \\ &z_{s+1}(T) = -1 \end{aligned} \tag{107}$$

From equations (106) and (107), one obtains $z_{s+1}(t) = -1$, and hence one has

$$H(x,z,\theta) = \sum_{i=1}^{s} z_i f_i(x;\theta) - \frac{dx_{s+1}}{dt} \tag{108}$$

All other relationships of equations (91) and (94) remain the same. This optimization problem can now be solved by using methods introduced in Section 2 for the case of a simple process, i.e., one involving no separating and combining points. Once the optimization calculation for Unit 1 is completed, the final values x(T) are obtained. These values provide the optimal initial values for Unit 2. The optimal policy for Unit 2 can be recovered by using equations (99) and (100).

So far a system whose first unit is optimized by employing the maximum principle has been dealt with. When the first unit in the sequence is not to be optimized by the maximum principle, the same procedure is still applicable. However, one must, in general, calculate a grid of values associated with the unit optimized by the maximum principle, since in this case the initial conditions of the units using the maximum principle are not given. Generally there are no given initial conditions for any unit except the first one. When the grid of value is obtained, the optimal policy of the units preceding this unit can be obtained by applying the principle of optimality. Note that if the unit which is to be optimized by using the maximum principle is a one-state variable process and the functional dependence of the optimal value with respect to the feed condition to this unit can be obtained analytically, the calculation of a grid of values is not necessary.

In what follows, two examples will be presented to illustrate the use of the method of sequential union. The examples are chosen so that the overall optimum can be obtained from the analytical solution without any calculation of a grid of values.

c. Tubular Flow Reactor Followed by a Multi-stage Cross-current Extraction Process

In this section a two-unit process which consists of a tubular reactor of length L_1 (continuous process) followed by a two-stage cross-current extractor (discrete process), as shown in Figure 11 is considered.

It is assumed that an autocatalytic reaction of the type

$$B \quad R \underset{k_2}{\overset{k_1}{\rightleftarrows}} R \quad R$$

takes place in the tubular reactor. The product stream is then fed to the liquid-liquid extractor for purification. It is assumed also that reactant B is immiscible in the solvent and only the product R is extracted. It is desired to maximize the over-all net profit by finding the optimal temperature profile along the tubular reactor and by allocating the optimal amount of washing water at each of the two extractors.

Unit 2 will be optimized first by using dynamic programming and then Unit 1 by the maximum principle. The over-all optimum is then obtained by use of the principle of optimality. The rate of the autocatalytic reaction can be written, with respect to production of reactant R, as

$$R_R = k_1 C_B{}^b \; C_R{}^r - k_2 C_R{}^s \tag{109}$$

where C_i is the molar concentration of component i; b and r are the order of reaction with respect to components B and R respectively in the forward reaction and s is the order of reaction of the reverse reaction. From the stoichiometry one has at every point along the reactor

$$C_0 = C_{B0} \quad C_{R0} = C_B \quad C_R$$

where C_{i0} is the initial molar concentration of reactant i. Therefore, equation (109) can be written as

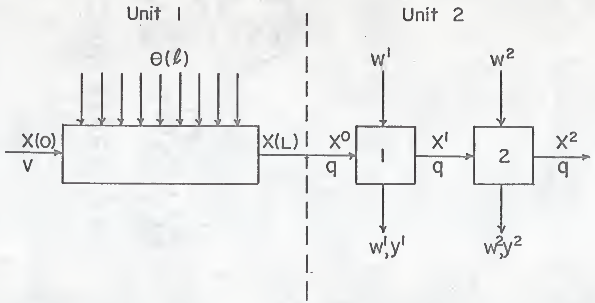

Fig.11 A schematic diagram for the process with a tubular reactor followed by a multistage cross-current liquid-liquid extraction.

$$R_R = k_1(C_0 - C_R)^b\, C_R{}^r - k_2 C_R{}^s$$

Rearranging the above equation, one obtains

$$R_R = k_1\ (1 - \frac{C_R}{C_0})^b\ (\frac{C_R}{C_0})^r (C_0)^{b+r} - k_2(\frac{C_R}{C_0})^s\ (C_0)^s \qquad (110)$$

The steady-state differential material balance for reactant R in the differential section $d\ell$ of reactor yields

$$\left\{\begin{array}{l}\text{Rate of input of component R at the inlet of}\\ \text{differential section } d\ell \text{ of the reactor line}\end{array}\right\}$$

$$- \left\{\begin{array}{l}\text{Rate of output of component R at the outlet of}\\ \text{differential section } d\ell \text{ of the reactor line}\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\text{Rate of production of component R in the}\\ \text{differential section } d\ell \text{ of the reactor line}\end{array}\right\}$$

$$= 0$$

i.e.

$$\{vC_R\} - \{vC_R \quad v\frac{dC_R}{d\ell}\, d\ell\} \quad A\, d\ell\{R_R\} = 0$$

or

$$\frac{dC_R}{d\ell} = \frac{A}{v}\ \{R_A\}$$

where v is the volumetric flow rate in the reactor and A is the cross-sectional area of the reactor.

Substituting equation (110) into this equation yields

$$\frac{dC_R}{d\ell} = \frac{A}{v} \left\lfloor k_1(1 - \frac{C_R}{C_0})^b\ (\frac{C_R}{C_0})^r\ (C_0)^{b+r} - k_2(\frac{C_R}{C_0})^s\ (C_0)^s \right\rfloor \qquad (111)$$

In terms of fractional molar concentration, $x_i = \frac{C_i}{C_0}$, one can rewrite equation (111) as

$$\frac{dx_1}{d\ell} = \frac{A}{v} \lfloor k_1\ (1 - x_1)^b (x_1)^r (C_0)^{b+r-1} - k_2 (x_1)^s (C_0)^{s-1} \rfloor \qquad (112)$$

where subscript 1 refers to reactant R (component 1). If one lets $C_0 = C_B + C_R = 1$, equation (112) can be replaced by

$$\frac{dx_1}{d\ell} = \frac{A}{v} \lfloor k_1\ (1 - x_1)^b (x_1)^r - k_2 (x_1)^s \rfloor \qquad (113)$$

This is the performance equation for this unit.

One derives the transformation equation of Unit 2 by considering it as an n-stage process (see Figure 12). The material balance with respect to product R around the nth stage gives [22]

$$w^n y^n = q(x_1^{n-1} - x_1^n) \qquad (114)$$

where w = wash water rate, lb/hr

y = composition of product R at the outlet of the extractor, dimensionless

$q = v\rho_m$, mass flow rate, lb/hr

ρ_m = density of mixture (assumed to be constant), $\frac{\text{lb}}{\text{ft}^3}$

or

$$u^n y^n = x_1^{n-1} - x_1^n \qquad (115)$$

where

$$u^n = w^n/q \qquad (116)$$

Let $Q_N = \sum_{n=1}^{N} w^n y^n = q(x_1^0 - x_1^N)$ be the total amount of R extracted and $G_N = \sum_{n=1}^{N} w^n$ be the total amount of washing water supplied. Then the net profit function for Unit 2 may be written as

$$P_N = Q_N - \lambda G_N \qquad (117)$$

where λ is the relative cost of washing water and it can be regarded as a

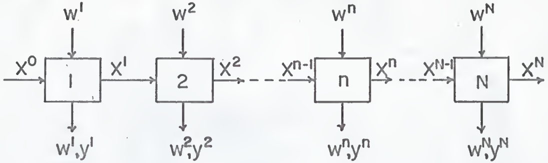

Fig.12 A schematic diagram of a multistage cross-current liquid liquid extraction.

Lagrange multiplier. Equation (117) is equivalent to

$$P_N = q \sum_{n=1}^{N} (x_1^{n-1} - x_1^n) - \lambda \sum_{n=1}^{N} w^n \tag{118}$$

Substitution of equation (116) into equation (118) gives

$$P_N = q \left\lfloor \sum_{n=1}^{N} (x_1^{n-1} - x_1^n) - \lambda \sum_{n=1}^{N} w^n \right\rfloor = q \sum_{n=1}^{N} u^n(y^n - \lambda) \tag{119}$$

which, together with equation (115) are the performance equations of Unit 2.

Now consider the return function of Unit 2. From equation (119), the return function of Unit 2 is

$$f_N(x_1^0) = \underset{\{u^n\}}{\text{Max}} \sum_{n=1}^{N} u^n(y^n - \lambda) \quad , \qquad x_1^0 = a \tag{120}$$

If a linear equilibrium relationship is assumed in each stage, the relation between the concentrations x^n and y^n is

$$x^n = \alpha y^n \tag{121}$$

Substituting equation (121) into equation (120) yields

$$f_N(a) = \underset{\{u^n\}}{\text{Max}} \sum_{n=1}^{N} u^n \left(\frac{x_1^n}{\alpha} - \lambda\right) \tag{122}$$

According to equation (99), one has the following recursive relation as

$$f_N(a) = \underset{u^1}{\text{Max}} \left\{u^1 \left(\frac{x_1^1}{\alpha} - \lambda\right) + f_{N-1}(x_1^1)\right\} \tag{123}$$

with $x_1^0 = a$ and $f_0(a) = 0$.

For a two-stage extraction process ($N = 2$), combining equations (115) and (121), gives for the second stage

$$x_1^2 = x_1^1 - u^2 y^2 = \alpha y^2$$

or

$$x_1^2 = \frac{\alpha x_1^1}{u^2+\alpha} \tag{124}$$

Equation (123) for $N = 2$ is

$$f_2(a) = \underset{u^1}{\text{Max}} \left\{u^1 \left(\frac{x_1^1}{\alpha} - \lambda\right) + f_1(x_1^1)\right\} \tag{125}$$

where

$$f_1(x_1^1) = \underset{u^2}{\text{Max}} \left\{u^2 \left(\frac{x_1^2}{\alpha} - \lambda\right) + f_0(x_1^0)\right\} \tag{126}$$

Substituting equation (124) into equation (126) and noting that $f_0(x_1^0) = 0$, one obtains

$$f_1(x_1^1) = \underset{u^2}{\text{Max}} \left\{u^2 \left(\frac{x_1^1}{\alpha+u^2} - \lambda\right)\right\} \tag{127}$$

Partially differentiating the quantity in the bracket of equation (127) with respect to u^2 and setting it equal to zero to solve for $\overline{u^2}$, one obtains

$$\overline{u^2} = \sqrt{\frac{x_1^1\alpha}{\lambda}} - \alpha \tag*{(128)*}$$

Substituting equation (128) into equation (124), one obtains

$$x_1^2 = \sqrt{\alpha x_1^1\lambda} \tag{129}$$

Substituting equation (128) into equation (127) gives

$$f_1(x_1^1) = x^1 - 2\sqrt{\alpha x_1^1\lambda} + \alpha\lambda \tag{130}$$

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* The upper bar indicates the optimal solution.

provided that $x_1^1 > \lambda\alpha$. This is the optimal interval return function for the second stage of the extraction process with respect to the outlet condition of the first stage. Similarly, for the first stage, applying equation (125), one has

$$f_2(a) = \underset{u^1}{\text{Max}} \left\{ u^1 \left(\frac{x_1^1}{\alpha} - \lambda\right) + f_1(x_1^1) \right\} \tag{131}$$

Substituting equation (130) into equation (131) yields

$$f_2(a) = \underset{u^1}{\text{Max}} \left\{ u^1 \left(\frac{x_1^1}{\alpha} - \lambda\right) + x_1^1 - 2\sqrt{\alpha x_1^1 \lambda} + \alpha\lambda \right\} \tag{132}$$

Combining equations (115) and (121), for n = 1, one has for the first stage

$$x_1^1 = x_1^0 - u^1 y^1 = \alpha y^1$$

or

$$x_1^1 = \frac{x_1^0 \alpha}{u^1 + \alpha} = \frac{a\alpha}{u^1 + \alpha} \tag{133}$$

Substituting equation (133) into equation (132) and simplifying the resulting equation, one obtains

$$f_2(a) = \underset{u^1}{\text{Max}} \left\{ a - u^1\lambda - 2\sqrt{\frac{(\alpha)^2 \lambda a}{u^1 \quad \alpha}} + \alpha\lambda \right\} \tag{134}$$

Partially differentiating the quantity in the bracket of equation (134) with respect to u^1 and setting it equal to zero to solve for $\overline{u^1}$, one obtains

$$\overline{u^1} = \left(\frac{(\alpha)^2 a}{\lambda}\right)^{\frac{1}{3}} - \alpha \tag{135}$$

Substituting equation (135) into equation (133) yields

$$x_1^1 = \lfloor \alpha\lambda(a)^2 \rfloor^{\frac{1}{3}} \tag{136}$$

Substituting equations (135) and (136) into equation (134), one has

$$f_2(a) = a - 3\lfloor (\alpha)^2(\lambda)^2 a \rfloor^{\frac{1}{3}} \quad 2\alpha\lambda \tag{137}$$

Substituting equation (136) into equation (128) and noting equation (135), one obtains the optimal policy for the two-stage extraction unit as

$$\overline{u^1} = \overline{u^2} = \left(\frac{(\alpha)^2 a}{\lambda}\right)^{\frac{1}{3}} - \alpha \tag{138}$$

This means that the wash water is divided equally between the two stages.

To obtain the optimum for the over-all process or the maximum combined profit from the reactor and purification sections, the objective function must be established for the entire process. Since no product R can be sold until it is purified, there is no direct return available from Unit 1. The operating cost for Unit 1 is assumed to be proportional to the amount of reactant B converted into the product R as

$$\beta(x_1(L) - x_1(0)) \tag{139}$$

where β is a proportionality constant and $x_1(L)$ and $x_1(0)$ are the fractional mass concentrations of R at the outlet and inlet of the reactor respectively.

Since the maximum profit from the purification section has already been established, the over-all net profit function can be written from equations (137) and (139) according to the principle of optimality as ⌊see equation (101)⌋

$$S = x_1^0 - 3\lfloor (\alpha)^2(\lambda)^2 x_1^0 \rfloor^{\frac{1}{3}} + 2\alpha\lambda - \beta\lfloor x_1(L) - x_1(0) \rfloor \tag{140}$$

Remembering that $x_1(L) = x_1^0$, one can rewrite equation (140) as

$$S = x_1(L) - 3\left\lfloor (\alpha)^2(\lambda)^2 x_1(L)\right\rfloor^{\frac{1}{3}} + 2\alpha\lambda - \beta\left\lfloor x_1(L) - x_1(0)\right\rfloor \qquad (141)$$

To find the decision function $\theta(\ell)$ which maximizes the objective function, one first introduces a second state variable x_2 defined as

$$x_2(\ell) = x_1(\ell) - 3\left\lfloor (\alpha)^2(\lambda)^2 x_1(\ell)\right\rfloor^{\frac{1}{3}} \quad 2\alpha\lambda - \beta\left\lfloor x_1(\ell) - x_1(0)\right\rfloor \qquad (142)$$

Differentiation of equation (142) with respect to ℓ gives

$$\frac{dx_2}{d\ell} = (1-\beta)\,\frac{dx_1}{d\ell} - (\alpha\lambda)^{\frac{2}{3}}\, x_1^{-\frac{2}{3}}\,\frac{dx_1}{d\ell} \qquad (143)$$

This equation and equation (113) form the complete set of performance equations for Unit 1. The initial conditions are

$$x_1(0) = \gamma \qquad (144)$$

$$x_2(0) = \gamma - 3\left\lfloor (\alpha)^2(\lambda)^2\gamma\right\rfloor^{\frac{1}{3}} + 2\alpha\lambda \qquad (145)$$

Substituting equation (113) into equation (143), one obtains

$$\frac{dx_2}{d\ell} = \left[1-\beta-(\alpha\lambda)^{\frac{2}{3}}\, x_1^{-\frac{2}{3}}\right]\left[k_1(1-x_1)^b(x_1)^r - k_2(x_1)^s\right]\frac{A}{v} \qquad (146)$$

According to equations (7) and (8), we can write the Hamiltonian H and the adjoint variables for this unit as

$$H = \frac{Az_1}{v}\left\lfloor k_1(1-x_1)^b(x_1)^r - k_2(x_1)^s\right\rfloor + \frac{Az_2}{v}\left\lfloor k_1(1-x_1)^b(x_1)^r - k_2(x_1)^s\right\rfloor$$

$$\cdot\left\lfloor 1-\beta-(\alpha\lambda)^{\frac{2}{3}}\,(x_1)^{-\frac{2}{3}}\right\rfloor \qquad (147)$$

$$\frac{dz_1}{d\ell} = - \frac{Az_1}{v} \left[bk_1(1-x_1)^{b-1}(x_1)^r + k_1(1-x_1)^b r(x_1)^{r-1} - k_2 s(x_1)^{s-1} \right]$$

$$- \frac{Az_2}{v} \left[bk_1(1-x_1)^{b-1}(x_1)^r + k_1(1-x_1)^b r(x_1)^{r-1} - k_2 s(x_1)^{s-1} \right]$$

$$\cdot \left[1-\beta-(\alpha\lambda)^{\frac{2}{3}} (x_1)^{-\frac{2}{3}} \right]$$

$$- \frac{Az_2}{v} \left[k_1(1-x_1)^b (x_1)^r - k_2(x_1)^s \right] \left[\frac{2}{3} x_1^{-\frac{5}{3}} (\alpha\lambda)^{\frac{2}{3}} \right] \tag{148}$$

$$\frac{dz_2}{d\ell} = 0 \tag{149}$$

Since the objective function is $x_2(L)$, we have $c_1 = 0$ and $c_2 = 1$. According to equation (95), one has

$$z_1(L) = 0 \tag{150}$$

$$z_2(L) = -1 \tag{151}$$

Combining equation (151) with equation (149) yields

$$z_2(\ell) = -1 \tag{152}$$

Substituting equation (152) into equation (147), one has

$$H = \frac{A}{v} \left[k_1(1-x_1)^b (x_1)^r - k_2(x_1)^s \right] \left\{ z_1 - \left[1-\beta-(\alpha\lambda)^{\frac{2}{3}} (x_1)^{-\frac{2}{3}} \right] \right\} \tag{153}$$

When the minimum of H occurs at the stationary point, one can obtain the optimal decision function $\theta(\ell)$ by partially differentiating equation (153) with respect to θ and setting it equal to zero, that is

$$\frac{\partial H}{\partial \theta} = \frac{A\left\{ z_1 - \left[1-\beta-(\alpha\lambda)^{\frac{2}{3}} (x_1)^{-\frac{2}{3}} \right] \right\}}{v} \left[(1-x_1)^b (x_1)^r \frac{dk_1}{d\theta} - (x_1)^s \frac{dk_2}{d\theta} \right] = 0$$

where $\frac{dk_1}{d\theta}$ and $\frac{dk_2}{d\theta}$ can be obtained by differentiating the equations

$$k_1 = k_{10}\, e^{-\frac{E_1}{R\theta}}$$

$$k_2 = k_{20}\, e^{-\frac{E_2}{R\theta}}$$

with respect to θ. One thus finally obtains the optimal temperature, $\theta(\ell)$, as

$$\bar{\theta}(\ell) = \left(\frac{E_1 - E_2}{R}\right) \frac{1}{\ln \left\lfloor \xi(x_1)^{r-s}(1-x_1)^b \right\rfloor} \tag{154}$$

where

$$\xi = \frac{k_{10}\ E_1}{k_{20}\ E_2}$$

Substituting equation (154) into equation (113) yields

$$\frac{dx_1}{d\ell} = \frac{A}{v} \Big\{ k_{10}(1-x_1)^b(x_1)^r \left\lfloor \xi(x_1)^{r-s}(1-x_1)^b \right\rceil^{\lambda_1}$$

$$- (x_1)^s k_{20} \left\lfloor \xi(x_1)^{r-s}(1-x_1)^b \right\rceil^{\lambda_2} \Big\} \tag{155}$$

where

$$\lambda_1 = \frac{E_1}{E_2 - E_1} \qquad \text{and} \qquad \lambda_2 = \frac{E_2}{E_2 - E_1}$$

In integrating equation (155) the activation energies are chosen in order that

$$\frac{E_2}{E_1} = 2 \qquad \text{or} \qquad \lambda_1 = 1 \qquad \text{and} \qquad \lambda_2 = 2 \tag{156}$$

It should be noted that equation (155) is valid for any value of E_1 and E_2. Equation (156) is chosen for the simplification of the problem.

Substituting equation (156) into equation (155) and simplifying the resulting equation, one obtains

$$\frac{dx_1}{d\ell} = \frac{A}{V} \left\lfloor k_{10}\xi - k_{20}(\xi)^2 \right\rfloor \left\lfloor (1-x_1)^{2b}(x_1)^{2r-s} \right\rfloor \tag{157}$$

If one assumes that the reaction is first order with respect to each component for the forward reaction and second order with respect to the reversible reaction, that is, $b = r = 1$ and $s = 2$, equation (157) can be integrated as

$$\frac{1}{1-x_1} = \frac{A\ell}{V} \left\lfloor k_{10}\xi - k_{20}(\xi)^2 \right\rfloor + C \tag{158}$$

The integration constant C is evaluated by using equation (144) as

$$\frac{1}{1-\gamma} = C \tag{159}$$

Substituting equation (159) into equation (158) yields

$$\ell = \frac{V}{A\xi(k_{10} - k_{20}\xi)} \left(\frac{1}{1-x_1} - \frac{1}{1-\gamma}\right) \tag{160}$$

Combining equations (154) and (160) one obtains the optimal policy for Unit 1.

Solving equation (160) for $x_1(L)$, one has

$$L = \frac{V}{A\xi(k_{10} - k_{20}\xi)} \left(\frac{1}{1-x_1(L)} - \frac{1}{1-\gamma}\right)$$

or

$$x_1(L) = \frac{\frac{V}{A}\gamma + L\xi(k_{10} - k_{20}\xi)(1-\gamma)}{\frac{V}{A} + L\xi(k_{10} - k_{20}\xi)(1-\gamma)} \tag{161}$$

Substituting equation (161) into equations (139) and (137) gives the optimal profit (or cost) for the reactor and the purification section respectively. The over-all optimal net profit is obtained by substituting equation (161) into equation (141).

d. Continuous Stirred Tank Reactor Followed by a Tubular Flow Reactor with Product Recycle to an Internal Point

In this section a chemical process consisting of a continuous stirred tank reactor followed by a tubular reactor with product recycle to an internal point, as shown in Figure 13, will be considered. Unit 2 (the tubular reactor) consists of four branches, the feed line of length L_1 (branch 1), the reactor of length L_2 (branch 2), the discharge line of length L_3 (branch 3), and the recycle line of length L_4 (branch 4) with volumetric flow rates of $v^{(1)}$, $v^{(2)}$, $v^{(3)}$, and $v^{(4)}$, respectively. In Unit 1 (CSTR), the volumetric flow rate and the volume of reactor are given as v and V respectively.

A first-order reversible chemical reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

is taking place in this series of reactors. It is desired to maximize the conversion of product B at the end of the tubular reactor by the proper manipulation of the temperature in the stirred tank reactor and the temperature profile along the tubular reactor.

First, the maximum principle is applied to optimize the tubular reactor unit and the over-all optimum is then obtained by the principle of optimality.

Let us establish the performance equations for both units as follows:

A steady-state material balance for the ith component over a CSTR is given by

$$\left\{\text{rate of input of the ith component}\right\} + \left\{\text{rate of production of the ith component}\right\} = \left\{\text{rate of output of the ith component}\right\}$$

that is,

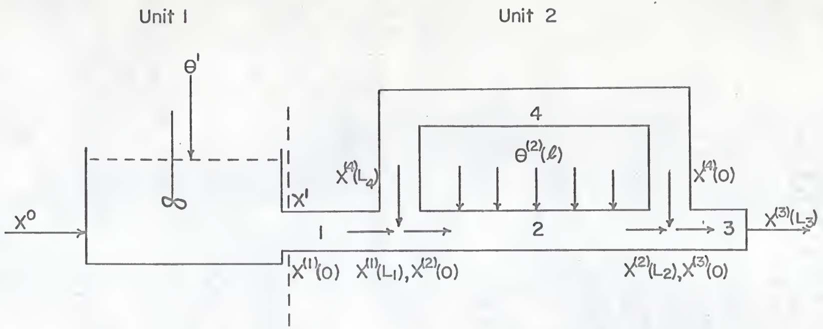

Fig.13 A schematic diagram for a process with a CSTR followed by a tubular reactor with product recycled to an internal point.

$$vC_i^0 + R_i V = vC_i^1 \qquad (162)^*$$

where

C_i^0 = inlet mass concentration of the ith component, $\frac{lb}{ft^3}$

C_i^1 = outlet mass concentration of ith component , $\frac{lb}{ft^3}$

v = total volumetric flow rate , $\frac{ft^3}{hr}$

R_i = mass reaction rate of production for ith component , $\frac{lb}{ft^3\text{-}hr}$

V = volume of reactor , ft^3

For the reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

in which both the forward and backward reaction are assumed to be first-order, the reaction rate R_B in terms of the production of component B is given by

$$R_B = k_1 C_A^1 - k_2 C_B^1 \qquad (163)$$

where the specific reaction rate k_i follows Arrhenius law as

$$\begin{aligned} k_1 &= k_{10}\, e^{-\frac{E_1}{R\theta^1}} \\ k_2 &= k_{20}\, e^{-\frac{E_2}{R\theta^1}} \end{aligned} \qquad (164)$$

where the reaction temperature θ^1 is the decision variable. All other notation is defined in Section 3a. Substitution of equation (163) into equation (162) for component B gives

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* Superscripts indicate the stage in Unit 1.

$$vC_B^0 + (k_1C_A^1 - k_2C_B^1)\ V = vC_B^1$$

Dividing the above equation by $v(C_A^1 \quad C_B^1)$, one obtains

$$\frac{C_B^0}{C_A^1+C_B^1} + (k_1\frac{C_A^1}{C_A^1+C_B^1} - k_2\frac{C_B^1}{C_A^1+C_B^1})\ \frac{V}{v} = \frac{C_B^1}{C_A^1+C_B^1}$$

Assuming that $C_A^0 + C_B^0 = C_A^1 + C_B^1$ is constant, and letting $\frac{V}{v} = t$, the preceding equation becomes

$$x_1^0 + t(k_1x_2^1 - k_2x_1^1) = x_1^1 \tag{165}$$

where

$$x_1^0 = \frac{C_B^0}{C_A^0+C_B^0}, \qquad x_1^1 = \frac{C_B^1}{C_A^1+C_B^1}, \qquad x_2^1 = \frac{C_A^1}{C_A^1+C_B^1}$$

In equation (165) x_1^1 and x_2^1 represent the fractional mass concentration of B and A respectively at the outlet of CSTR and t is the holding time in the reactor.

Since $x_1^1 + x_2^1 = 1$, equation (165) can be replaced by

$$x_1^1 = \frac{x_1^0 + k_1(\theta^1)\ t}{1 + t\lfloor k_1(\theta^1)+k_2(\theta^1)\rfloor} \tag{166}$$

Equation (166) is the performance equation for Unit 1.

A steady state material balance with respect to component B over a differential section $d\ell$ in branch 2 of Unit 2 leads to (see Section 4c)

$$\frac{dx_1^{(2)}}{d\ell} = -\frac{A^{(2)}}{v^{(1)}+v^{(4)}}\lfloor (k_1\ k_2)\ x_1^{(2)} - k_1\rfloor \tag{167}$$

where $A^{(2)}$ = cross sectional area of tubular reactor (Branch 2)

$v^{(1)}$ = volumetric flow rate of feed line

$v^{(4)}$ = volumetric flow rate of recycle line

Since no transformation is taking place and no control action is imposed on branches 1, 3, and 4, one has the following performance equations

$$\frac{dx_1^{(1)}}{d\ell} = \frac{dx_1^{(3)}}{d\ell} = \frac{dx_1^{(4)}}{d\ell} = 0 \tag{168}$$

for the feed, discharge and recycle lines, respectively.

The initial state of Unit 2 is, according to the above equation

$$x_1^{(1)}(0) = x_1^{(1)}(L_1) = x_1^{1} \tag{169}$$

Conservation of mass at the combining point requires the junction equation to be

$$v^{(2)}x_1^{(2)}(0) = v^{(1)}x_1^{(1)}(L_1) + v^{(4)}x_1^{(4)}(L_4)$$

or

$$x_1^{(2)}(0) = \alpha x_1^{(1)}(L_1) + \beta x_1^{(4)}(L_4) \tag{170}$$

where

$$\alpha = \frac{v^{(1)}}{v^{(1)}+v^{(4)}}\, , \qquad \beta = \frac{v^{(4)}}{v^{(1)}+v^{(4)}}$$

The junction equations at the separating point are

$$\begin{aligned} x_1^{(3)}(0) &= x_1^{(2)}(L_2) \\ x_1^{(4)}(0) &= x_1^{(2)}(L_2) \end{aligned} \tag{171}$$

By substituting equations (168), (169), and (171) into equation (170) one obtains

$$x_1^{(2)}(0) = \alpha x_1^{1} + \beta x_1^{(2)}(L_2) \tag{172}$$

It is desired to maximize the yield of product B, that is, to maximize the objective function

$$S = x_1^{(3)}(L_3) - x_1^0$$

$$= x_1^{(2)}(L_2) - x_1^0 \tag{173}$$

The objective function in equation (173) can be written as

$$S = (x_1^1 - x_1^0) + (x_1^{(2)}(L_2) - x_1^1)$$

$$= S_1 + S_2$$

where

$$S_1 = x_1^1 - x_1^0 \tag{174}$$

$$S_2 = x_1^{(2)}(L_2) - x_1^1 \tag{175}$$

One can consider that S_1 and S_2 are the interval profits from Unit 1 and Unit 2 respectively. Thus the problem becomes one of maximizing the total profit $(S_1 + S_2)$ by a proper choice of the temperature in the CSTR and the tubular reactor. According to equation (99), one can write the recursive relation as

$$g_2(x_1^0) = \underset{\theta^1}{\mathrm{Max}} \left\lfloor S_1(x_1^0;\theta^1) + g_1(x_1^1) \right\rfloor \tag{176}$$

where

$$g_1(x_1^1) = \underset{\theta^{(2)}(\ell)}{\mathrm{Max}} \left\lfloor S_2(x_1^1;\theta^{(2)}(\ell)) \right\rfloor = \underset{\theta^{(2)}(\ell)}{\mathrm{Max}} \left\lfloor x_1^{(2)}(L_2) - x_1^1 \right\rfloor \tag{177}$$

Unit 2 will be optimized first by using the maximum principle and the over-all optimum can then be obtained by the use of equation (176). In optimizing Unit 2, one considers the feed concentration to the tubular reactor to be given, for the time being; that is, $x_1^1 = a =$ constant.

Thus, maximizing the interval profit represented in equation (175) is equivalent to maximizing $x_1^{(2)}(L_2)$. By this consideration, the optimization of Unit 2 reduces to the problem of a simple recycle process.

According to equations (7) and (8), one has

$$H^{(1)} = H^{(3)} = H^{(4)} = 0 \tag{178}$$

$$H^{(2)} = - \frac{A^{(2)}}{v^{(1)} + v^{(4)}} \lfloor (k_1+k_2)\ x_1^{(2)} - k_1 \rfloor\ z_1^{(2)} \tag{179}$$

$$\frac{dz_1^{(1)}}{d\ell} = \frac{dz_1^{(3)}}{d\ell} = \frac{dz_1^{(4)}}{d\ell} = 0 \tag{180}$$

$$\frac{dz_1^{(2)}}{d\ell} = \frac{A^{(2)}}{v^{(1)} + v^{(4)}} (k_1+k_2)\ z_1^{(2)} \tag{181}$$

Since the objective function is $x_1^{(2)}(L_2)$, one has $c_1^{(2)} = 1$. Thus, at the final point,

$$z_1^{(2)}(L_2) = -1 \tag{182}$$

If one assumes that the minimum of H occurs at the stationary point ($\theta^{(2)}(\ell)$ is not constrained), one can determine the optimal temperature profile by taking the partial derivative of H with respect to θ and setting it equal to zero. Thus, from equation (179), one obtains

$$\frac{\partial H^{(2)}}{\partial \theta^{(2)}} = - \frac{A^{(2)} z_1^{(2)}}{v^{(1)} + v^{(4)}} \lfloor \left(\frac{dk_1}{d\theta^{(2)}} + \frac{dk_2}{d\theta^{(2)}}\right) x_1^{(2)} - \frac{dk_1}{d\theta^{(2)}} \rfloor = 0 \tag{183}$$

where

$$\frac{dk_1}{d\theta^{(2)}} = \frac{k_{10}\ E_1}{R(\theta^{(2)})^2}\ e^{-\frac{E_1}{R\ \theta^{(2)}}} \tag{184}$$

$$\frac{dk_2}{d\theta^{(2)}} = \frac{k_{20}\ E_2}{R(\theta^{(2)})^2}\ e^{-\frac{E_2}{R\ \theta^{(2)}}} \tag{184a}$$

Solving equation (183) for $\theta^{(2)}$ yields

$$\overline{\theta^{(2)}}(\ell) = \frac{E_2 - E_1}{R\ \ln\left(\xi\ \frac{x_1^{(2)}}{1-x_1^{(2)}}\right)} \tag{185}$$

where

$$\xi = \frac{k_{20}\ E_2}{k_{10}\ E_1}$$

Substitution of equation (185) into equation (167) yields

$$\frac{dx_1^{(2)}}{d\ell} = - \frac{A^{(2)}}{v^{(1)}\ v^{(4)}} \cdot \frac{k_{10}\xi^{-\lambda_1}(1-x_1^{(2)})^{\lambda_1+1}(x_1^{(2)})^{\lambda_2-1} - k_{20}\xi^{-\lambda_2}(1-x_1^{(2)})^{\lambda_2}(x_1^{(2)})^{\lambda_1}}{(x_1^{(2)})^{\lambda_1+\lambda_2-1}} \tag{186}$$

where

$$\lambda_1 = \frac{E_1}{E_2-E_1}, \qquad \lambda_2 = \frac{E_2}{E_2-E_1} \tag{187}$$

In the integration of equation (186), the activation energies of the forward and backward reactions have been chosen such that

$$\frac{E_2}{E_1} = 2$$

or

$$\lambda_1 = 1, \qquad \lambda_2 = 2 \tag{188}$$

Substituting these values of λ_i into equation (186), and performing the integration, one obtains

$$\frac{v^{(1)}+v^{(4)}}{A^{(2)}(k_{10}\xi^{-1} - k_{20}\xi^{-2})}\left\lfloor\frac{1}{1-x_1^{(2)}} + \ln(1-x_1^{(2)})\right\rfloor = \ell \quad C \tag{189}$$

One evaluates the integration constant C by the use of the initial condition given in equation (172). Thus,

$$C = \frac{v^{(1)}+v^{(4)}}{A^{(2)}(k_{10}\xi^{-1} - k_{20}\xi^{-2})}\left\{\frac{1}{1-\lfloor(\alpha x_1^1+\beta x_1^{(2)}(L_2)\rfloor} \quad \ln\lfloor 1-(\alpha x_1^1+\beta x_1^{(2)}(L_2))\rfloor\right\} \tag{190}$$

Substitution of the above equation into equation (189) yields

$$\frac{v^{(1)}+v^{(4)}}{A^{(2)}(k_{10}\xi^{-1} - k_{20}\xi^{-2})}\left\{\frac{1}{1-x_1^{(2)}} + \ln(1-x_1^{(2)}) - \frac{1}{1-\lfloor\alpha x_1^1+\beta x_1^{(2)}(L_2)\rfloor}\right.$$

$$\left. - \ln\left\lfloor 1-(\alpha x_1^1+\beta x_1^{(2)}(L_2))\right\rfloor\right\} = \ell \tag{191}$$

Equation (191) indicates the optimal concentration along the tubular reactor. At the end of the reactor, that is, at $\ell = L_2$, equation (191) involves only one unknown, $x_1^{(2)}(L_2)$. It is seen that equation (191) cannot be solved explicitly for $x_1^{(2)}(L_2)$. In other words, one cannot express $g_1(x_1^1)$ $\lfloor$see equation (177)$\rfloor$ explicitly as a function of $x_1^{(2)}(L_2)$ or x_1^1. The optimum value of $x_1^{(2)}(L_2)$ with regard to x_1^1, the inlet condition of Unit 2, is implicitly given by the following equation

$$C' \left\{\frac{1}{1-\bar{y}} + \ln(1-\bar{y}) - \frac{1}{1-(\alpha x_1^1+\beta\bar{y})} - \ln\left\lfloor 1-(\alpha x_1^1+\beta\bar{y})\right\rfloor\right\} - L_2 = 0 \tag{192}$$

or

$$F\,(x_1^1,\bar{y}) = 0 \tag{193}$$

where $\bar{y}$ represents the optimum value of $x_1^{(2)}(L_2)$ and

$$C' = \frac{v^{(1)} + v^{(4)}}{(k_{10}\xi^{-1} - k_{20}\xi^{-2})A^{(2)}}$$

Hence, one finally has

$$g_1(x_1^1) = \underset{\theta^{(2)}(\ell)}{\mathrm{Max}} \left\lfloor x_1^{(2)}(L_2) - x_1^1 \right\rfloor = \bar{y} - x_1^1 \tag{194}$$

For the optimization of Unit 2, x_1^1 was considered as a given initial condition. The functional interdependence $g_1(x_1^1)$ is implicitly given by equation (192) or (193). Substituting equations(174) and (194) into equation (171), one obtains

$$g_2(x_1^0) = \underset{\theta^1}{\mathrm{Max}} \left\lfloor x_1^1 - x_1^0 + \bar{y} - x_1^1 \right\rfloor = \underset{\theta^1}{\mathrm{Max}} \left\lfloor \bar{y} - x_1^0 \right\rfloor \tag{195}$$

The quantity in the bracket is a function of θ^1 and x_1^0, because $\bar{y}$ is a function of x_1^1 which, in turn, is a function of θ^1 as represented in equation (166). These functional relationships will be denoted as

$$G(x_1^0;\theta^1) = \bar{y} - x_1^0$$

When the maximum value of $G(x_1^0;\theta^1)$ occurs at the stationary point with respect to θ^1, the optimal value of θ^1 can be obtained by setting

$$\frac{\partial G}{\partial \theta^1} = \frac{d\bar{y}}{dx_1^1} \cdot \frac{dx_1^1}{d\theta^1} = 0 \tag{196}$$

One evaluates $\frac{d\bar{y}}{dx_1^1}$ by

$$\frac{d\bar{y}}{dx_1^1} = - \frac{\frac{\partial F}{\partial x_1^1}}{\frac{\partial F}{\partial \bar{y}}} \tag{197}$$

According to equation (197), one obtains from equation (192)

$$\frac{\partial F}{\partial x_1^1} = -C' \frac{\alpha(\alpha x_1^1+\beta\bar{y})}{\left[1-(\alpha x_1^1+\beta\bar{y})\right]^2}$$

$$\frac{\partial F}{\partial \bar{y}} = C' \frac{\bar{y}\left[1-(\alpha x_1^1+\beta\bar{y})\right]^2 - \beta(1-\bar{y})^2(\alpha x_1^1+\beta\bar{y})}{(1-\bar{y})^2\left[1-(\alpha x_1^1+\beta\bar{y})\right]^2}$$

Substituting the preceding two equations into equation (197), one obtains

$$\frac{d\bar{y}}{dx_1^1} = \frac{\alpha(1-\bar{y})^2(\alpha x_1^1+\beta\bar{y})}{\bar{y}\left[1-(\alpha x_1^1+\beta\bar{y})\right]^2 - \beta(1-\bar{y})^2(\alpha x^1+\beta\bar{y})} \tag{198}$$

Differentiating equation (166) with respect to θ^1 yields

$$\frac{dx_1^1}{d\theta^1} = \frac{\frac{dk_1}{d\theta^1} t + (t)^2 \left(k_2 \frac{dk_1}{d\theta^1} - k_1 \frac{dk_2}{d\theta^1}\right)}{\left[1+(k_1+k_2)t\right]^2}$$

Recalling that the functions $k_1(\theta^1)$ and $k_2(\theta^1)$ are given in equation (164), the differentiation of the preceding equation would become

$$\frac{dx_1^1}{d\theta^1} = \frac{\frac{tk_{10}}{R(\theta^1)^2}\left[E_1 e^{-\frac{E_1}{R\theta^1}} + tk_{20}(E_1-E_2)e^{-\frac{E_1+E_2}{R\theta^1}}\right]}{\left[1+k_1(\theta^1) + k_2(\theta^1)t\right]^2} \tag{199}$$

Substituting equations (198) and (199) into equation (196) yields

$$\frac{\partial G}{\partial \theta^1} = \frac{tk_{10}\left[E_1 e^{-\frac{E_1}{R\theta^1}} - tk_{20}(E_2-E_1)\, e^{-\frac{E_1+E_2}{R\theta^1}}\right]}{R(\theta^1)^2\left[1+(k_1+k_2)t\right]^2} \tag{200}$$

$$\cdot \frac{\alpha(1-\bar{y})^2(\alpha x_1^1+\beta\bar{y})}{\bar{y}\left[1-(\alpha x_1^1+\beta\bar{y})\right]^2 - \beta(1-\bar{y})^2(\alpha x_1^1+\beta\bar{y})} = 0$$

Since $\alpha x_1^1+\beta\bar{\bar{y}} \neq 0$ and $1-\bar{\bar{y}} \neq 0$ for any conversion less than 100 per cent, the only possibility for equation (200) to be equal to zero is

$$\theta^1 = \infty$$

or

$$E_1 e^{-\frac{E_1}{R\theta^1}} - tk_{20}(E_2-E_1)e^{-\frac{E_1+E_2}{R\theta^1}} = 0$$

When the value of temperature must be finite, the latter case would give the optimal temperature as

$$\overline{\theta^1} = -\frac{E_2}{R \ln \left(\frac{\lambda_1}{tk_{20}}\right)} \tag{201}$$

where t is the holding time in Unit 1 defined as $\frac{V}{v}$ and $\lambda_1 = \frac{E_1}{E_2-E_1}$.

It can be shown that equation (201) gives the same optimal temperature as one will have for a single CSTR. Thus, the optimal decision to be made at the CSTR remains the same or, in other words, it is independent of the downstream condition. This is actually observed from equation (200). Equating equation (200) to zero is equivalent to equating equation (199) to zero, which yields the optimal decision for a single CSTR.

One comes to the conclusion that the optimal policy for this two-unit system is to choose the temperature which will maximize the outlet concentration of Unit 1, and let this outlet concentration be the given inlet condition of Unit 2 and then maximize the outlet concentration of Unit 2 by the proper choice of temperature along the tubular reactor. These facts may also be verified by the following reasoning. Equation (198) indicates how x_1^1 affects the optimal final concentration $\bar{\bar{y}}$. Equation (189) indicates that 100% conversion ($x_1^{(2)} = 1$) gives rise to a reactor with infinite length, that is, the conversion must be less than 100%. Therefore, the following inequality must hold for the numerator of equation (198)

$$\alpha(1-\bar{y})^2(\alpha x_1^1+\beta\bar{y}) > 0 \tag{202}$$

Furthermore, we have $\bar{y} > (\alpha x_1^1+\beta\bar{y})$ and $\beta \leq 1$; hence, the following inequality must hold for the denominator of equation (198)

$$\bar{y}\left[1-(\alpha x_1^1+\beta\bar{y})\right]^2 > \beta(1-\bar{y})^2(\alpha x_1^1+\beta\bar{y}) \tag{203}$$

Since both the numerator and denominator of equation (198) are positive, one has the following inequality

$$\frac{d\bar{y}}{dx_1^1} > 0$$

In other words, $\bar{y}$ is an increasing function with respect to x_1^1. In order to obtain a higher value of $\bar{y}$, one must have a higher value of x_1^1 regardless of the operating policy in Unit 2. This simple but surprising result appears to be a consequence of the characteristics of the reversible reaction $A \rightleftarrows B$ and the objective function of the process under consideration or is a consequence of the general result that the optimal policy with a single state variable is always disjoint [11].

The numerical data chosen for the calculation of equations (166), (185), and (191) are

$A^{(2)} = 1$ ft^2

$k_{10} = 2.51 \times 10^5$ hr^{-1}

$k_{20} = 1.995 \times 10^7$ hr^{-1}

$E_1 = 10{,}000$ Btu/lb-mol

$E_2 = 20{,}000$ Btu/lb-mol

$$v^{(1)} = 1{,}000 \text{ ft}^3/\text{hr}$$

$$t = 2.5 \times 10^{-3} \text{ hr}$$

$$x_1{}^0 = 0$$

$$L_2 = 10 \text{ ft}$$

$$R = 2 \frac{\text{Btu}}{\text{lb-mole } ^\circ\text{R}}$$

From equation (201), the optimal temperature in the CSTR is calculated as

$$\overline{\theta^1} = 930.4 \ ^\circ\text{R}$$

With this temperature, the optimum outlet concentration from the CSTR is calculated according to equation (166) to be

$$x_1^1 = 0.583$$

Substituting the above optimal feed condition of the tubular reactor into equation (191), and solving for $x_1^{(2)}$ by trial and error, one obtains the optimal concentration profiles along the reactor. The optimum final product thus obtained without recycle is

$$\bar{y} = 0.916$$

The optimal temperature profiles along the reactor can be recovered from equation (185). The results of calculations with a fractional recycle rate β as the parameter are shown in Figure 14. In dealing with equation (191), values of $v^{(4)}$ are calculated according to various values of β chosen.

It is worthwhile to mention that the optimal solution obtained can be verified by the perturbation technique. This is accomplished by investigating the vicinity of the optimal decision to see if it increases the value of the objective function. For this problem, the following check by perturbation shown in Table 3 has been made. In this table, the values of $x_1^{(2)}(L_2)$ in Rows a1 and b1 are the optimal values for $\beta = 0$ and $\beta = 0.5$

respectively.

It is also wroth mentioning that the optimal temperature obtained from equation (201) for the CSTR is essentially the same as the optimal temperature at the inlet of the tubular reactor without product recycle, as given by equation (185). This again shows the disjoint character of optimal temperature for the reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, that is, the temperature should always be chosen so that the rate of reaction will be as large as possible.

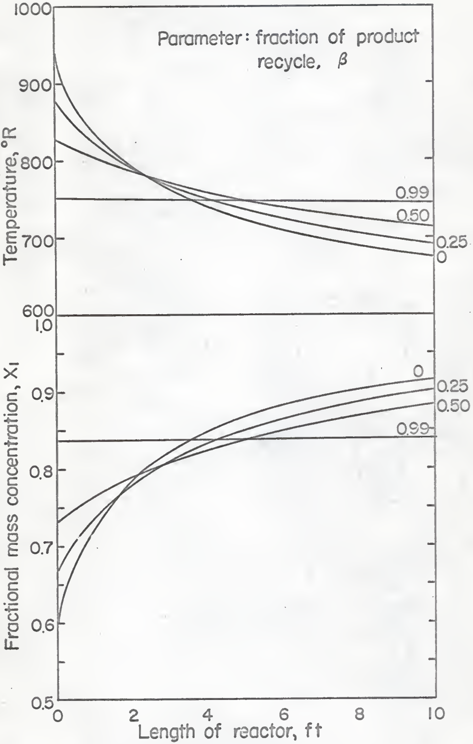

Fig.14 Optimal temperature and concentration profiles in a tubular reactor with product recycle for the reaction $A \underset{k2}{\overset{k1}{\rightleftharpoons}} B$.

Table 3. Perturbation check for the results of Section 4d

		θ^1(°R)	x_1^1	$x_1^{(2)}(L_2)$
$\beta = 0$	a1	930.4	0.583	0.9161
	a2	910	0.5815	0.9158
	a3	960	0.5814	0.9156
$\beta = 0.5$	b1	930.4	0.583	0.883
	b2	880	0.568	0.881
	b3	980	0.575	0.882

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NOMENCLATURE

A	chemical specie
$A^{(k)}$	cross sectional area of a tubular reactor in the kth branch
b	order of reaction
B	chemical specie
c_i	constant in objective function
C	chemical specie
C_i	concentration of component i
E_i	activation energy
f	number of final points
f_i	performance function
f_N	optimum value of the objective function for a N-stage process in Section 4c
g	function of state variable associated with separating point
g_N	optimum value of the objective function for a N-stage process
G_N	total amount of washing water supplied
h	interval profit function
H	the Hamiltonian function
k	branch number
k_i	specific reaction constant
k_{i0}	frequency factor
ℓ	independent variable, axial distance along a tubular reactor
L_k	total length of the kth branch tubular reactor
	final value of independent variable at the kth branch
n	the nth stage, total number of branches
N	total number of stages

P	net profit function
q	mass flow rate
Q_N	total amount of product R extracted
r	dimension of decision vector in Section 2a and Section 4b, order of reaction with respect to R in Section 4c
R	chemical specie or gas constant
R_i	rate of production of component i
s	dimension of state vector, order of reaction with respect to R in
t	the reverse reaction of an autocatalytic reaction
S	objective function
S_i	objective function of the ith unit
t	independent variable, time or position; holding time in Section 3a and Section 3b
T	final value of independent variable t
T_k	final value of independent variable t at the kth branch
u^n	w^n/q
$v^{(k)}$	volumetric flow rate in the kth branch
V	volume of a continuous stirred tank reactor
w^n	washing water flow rate into the nth stage
x	state vector
x_i	molar concentration of component i in Section 3a and Section 3b
y^n	composition of extract at outlet of the nth extractor
$\bar{y}$	optimum value of a state variable at the end of a tubular reactor
z	adjoint vector

Greek Letters

α	initial value of a state vector in Section 4b; proportionality constant of equilibrium relation in Section 4c; fractional amount of feed stream in Section 4d
α_i	initial condition of state variable x_i
β	fractional amount of recycle stream in Section 4d
β_i	initial condition of x_i in the intermediate feed
γ_1	volumetric flow rate fraction of the feed stream
γ_2	volumetric flow rate fraction of the intermediate feed stream
η_i	dimensionless holding time in the ith reactor
$\eta_i^{(k)}$	closer approximation to the correct values of $x_i^{(k)}$
θ	decision vector
$\bar{\theta}$	the optimum value of θ
λ_1	E_1/E_2-E_1
λ_2	E_2/E_2-E_1
ξ	$k_{10}E_1/k_{20}E_2$
$\xi_i^{(k)}$	better approximate vale of $x_i^{(k)}(T_k)$ in the Runge-Kutta method
ρ_m	density of a mixture

OPTIMAL DESIGN OF FLOW CHEMICAL REACTORS WITH COMPLEX GEOMETRY

by

DANIEL YAW-CHUNG KO

B.S., National Taiwan University, 1962

AN ABSTRACT OF A MASTER'S THESIS

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The main purpose of this work is to show how the maximum principle and dynamic programming can be applied to topologically complex chemical rate processes, particularly to flow type chemical reactor systems. The study which treats four examples in detail consists of two parts.

The first part is an investigation of optimal temperature profiles in a series of plug flow reactors with either fresh feed fed to or intermediate product withdrawal from an internal point by using the maximum principle. For both examples, it is assumed that a first-order consecutive reaction $A \longrightarrow B \longrightarrow C$ is taking place in the reactors. The split type two-point-boundary value problems, which are encountered, are solved numerically by using an iterative Runge-Kutta method and backward integration. In the case of intermediate product withdrawal, it is found that the optimal temperature profile in the second reactor is almost flat, i.e. isothermal operation in the second reactor will meet the optimum condition. For the case of intermediate fresh feed, the effects of fractional amounts of the intermediate fresh feed on the optimal temperature profile are also studied.

The second part deals with the combined use of the maximum principle and dynamic programming. General working equations and computational schemes for a sequential union of these two methods are developed. It is found that the combined use of these two modern optimization techniques offers many advantages over either one of these two methods, particularly to the geometrically complex heterogeneous processes. To illustrate the use of these equations, two examples are worked out in detail.

In the first example a tubular flow reactor followed by a multistage cross-current extraction process is considered. An autocatalytic reaction is considered in the reactor. The working equations are derived for an objective function which maximizes total net profit. This profit is maximized

by the optimal choice of the temperature profile in the tubular reactor and by the optimal allocation of washing water in the cross-current extraction towers.

The second example consists of a continuous flow stirred tank reactor followed by a tubular flow reactor with product recycle to an internal point. A first order reversible reaction is assumed to take place in the reactors. Optimal temperatures in the CSTR and along the tubular reactor are determined in order to maximize the concentration of the desired final product. The effects of recycle to an internal point are also investigated.